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Bilge Water Membrane Treatment Phenomena Study

A.Y. Tremblay

M. Nottegar

Department of Chemical Engineering
University of Ottawa

Defence R&D Canada

Contractor Report

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Authors

A. Y. Tremblay and M. Nottegar

Approved by

D. Veinot

Contract Scientific Authority

Approved for release by

Walter E. Ellis

Chair, DREA Document Review Panel

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P515557.PDF [Page: 6 of 154]

BILGE WATER MEMBRANE TREATMENT PHENOMENA STUDY

REPORT

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BY

A.Y. Tremblay and M. Nottegar
Department of Chemical Engineering
University of Ottawa

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Bilge Water Membrane Treatment Phenomena Study

A. Y. Tremblay and M. Nottegar
University of Ottawa
161 rue Louise-Pasteur
CP 450 Succ. A
Ottawa ON Canada
K1N 6N5

ABSTRACT

This study is aimed at determining the phenomena that affect the treatment of bilge water using membrane based oily water separators. The results of the study are presented here as two separate papers. One paper discusses the most problematic particle sizes in the treatment of bilge water by synthetic membrane technologies while the other discusses the effects of shear and settling on bilge water treatment by ultrafiltration. The report also contains a section on the use of ultrafiltration membranes in oily water separators that elucidates the effects of small particles of soot in the bilge water on membrane performance and showed that the permeation of water through the membrane was entirely cake/gel limited. The thickness or resistance of this cake/gel layer was influenced by the quantity and size distribution of these soot particles in the influent stream. The work identifies the most effective membrane pore size to use in purifying bilge water which is contaminated with used diesel lubricating oil.

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Étude des conséquences du traitement de l'eau de fond de cale par les techniques membranaires

A.Y. Tremblay et M. Nottegar
Université d'Ottawa
161, rue Louise-Pasteur
C.P. 450, Succursale A
Ottawa (Ontario) Canada
K1N 6N5

RÉSUMÉ

Le but de la présente étude est de déterminer les conséquences du traitement de l'eau de cale au moyen de séparateurs à membrane conçus pour traiter les eaux mazouteuses. Les résultats de cette étude ont fait l'objet de deux publications distinctes. Le premier article traite de la taille des particules posant le plus de problèmes lors du traitement de l'eau de cale en appliquant les techniques de membranes synthétiques alors que le deuxième porte sur les effets du cisaillement et de la décantation sur le traitement de l'eau de cale par ultrafiltration. Le présent rapport renferme également une section portant sur l'utilisation des membranes d'ultrafiltration dans les séparateurs à eaux mazouteuses qui met en lumière les répercussions des petites particules de suie contenues dans l'eau de cale sur le comportement des membranes. Cette section montre également que la perméation de l'eau à travers la membrane est entièrement limitée par le gâteau et le gel. La quantité et la distribution granulométrique de ces particules de suie dans le cours d'eau infiltrant influent sur l'épaisseur ou la résistance du gâteau ou du gel. L'étude a mis en évidence la taille des pores de membrane la plus efficace devant être utilisée pour purifier l'eau de fond de cale contaminée par l'huile lubrifiante pour moteur à diesel.

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K1N 6N5

EXECUTIVE SUMMARY

Introduction

In an effort to meet stringent regulations on the level of oil contamination in waters discharged overboard into the ocean from the bilges of CF ships, the Canadian navy has equipped its warships with membrane based oily water separators. The treatment of bilge water aboard ships using membrane technologies is a challenging separation process because of the nominal composition of bilge water which contains a mixture of various oils, detergents, dissolved solids and fine particulate matter.

Principle Results

This report describes work conducted on a specially built apparatus to study the effect of various parameters on membrane performance. The most significant finding was that bilge water contaminated with used diesel lubricating oil, which is most often the case on board ship, is significantly more difficult to process than bilge water contaminated with unused lubricating oil or diesel fuel oil. This was due to the presence of small, (70 to 100 nanometer radius) carbonaceous soot particles that result from the combustion process which irreversibly block the membrane pores and resulted in greatly reduced permeate flux or throughput

Significance of Results

These findings explained the difficulties presently affecting the performance of the recently installed HYDROMEM oily water separators on CF ships. Further the results indicate that the HYDROMEM membrane system has the capability of producing permeate of the required purity but that the useful operational life of the membrane elements may be significantly decreased owing to loss of permeate flux

Future Plans

Given that the individual membrane elements are very costly to replace some form of influent pretreatment such as homogenization or shearing may be useful to affect the size of the carbonaceous debris that fouls the membranes in actual use and plans are therefore in place to conduct experiments to address this.

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A.Y. Tremblay et M. Nottegar
Université d'Ottawa
161, rue Louise-Pasteur
C.P. 450, Succ. A
Ottawa (Ontario) Canada
K1N 6N5

SOMMAIRE

Introduction

Dans un soucis de respecter la réglementation rigoureuse sur le niveau de contamination par l'huile des eaux de fond de cale déversées par les navires des Forces canadiennes dans l'océan, la Marine canadienne a équipé ses navires de guerre de séparateurs à membrane des eaux mazouteuses. Le traitement de l'eau de fond de cale effectué à bord des navires à l'aide des techniques membranaires est un procédé de séparation très délicat en raison de la composition nominale de l'eau de fond de cale qui contient un mélange d'huiles, de détergents, de matières solides dissous et de fines particules de nature diverse.

Principaux résultats

Le présent rapport décrit les travaux réalisés sur un appareil construit spécialement pour étudier les effets de divers paramètres sur le comportement des membranes La découverte la plus importante est que l'eau de cale contaminée par l'huile lubrifiante usée pour moteur à diesel, ce qui est le cas le plus fréquent sur les navires, est beaucoup plus difficile à traiter que celle contaminée par de l'huile lubrifiante non usée ou par du gas-oil. Ce phénomène est attribuable à la présence de petites particules de suie carbonée (70 à 100 nanomètre de rayon) provenant de la combustion et qui bloque irrévocablement les pores de la membrane, ce qui a pour effet de produire un flux de perméation ou un débit très réduit

Portée des résultats

Ces résultats font la lumière sur les difficultés affectant présentement les performances des séparateurs d'eau mazouteuse HYDROMEM récemment installés sur les navires des Forces canadiennes. Ils révèlent en outre que le système de membranes HYDROMEM peut produire une perméation de la pureté requise, mais que la vie opérationnelle utile des éléments de la membrane peut être considérablement réduite par la perte de l'écoulement du flux de perméation

Futurs programmes mis en place

Compte tenu que le remplacement des éléments d'une membrane est une opération très coûteuse, une méthode de prétraitement des affluents, telle que l'homogénéisation ou le cisaillement, pourrait influer positivement sur la taille des détritus carbonés qui souillent les membranes actuellement utilisées; des programmes sont par conséquent en place pour mener des expériences afin de résoudre ce problème.

SUMMARY

This study is aimed at determining the phenomena that affect the treatment of bilge water using membrane based oily water separators (OWS). The ultimate goal of this work is to obtain design criteria and support information for membrane based OWS to be used onboard HMC ships. These multiple objectives have produced both papers and shorter contributions that can be incorporated into future publications. Both are included as sections in this report. This reporting approach was mutually agreed upon with the scientific authority in order to facilitate the dissemination of this work.

The report is divided into the following sections:

SECTION 1 Two papers with a fairly common introduction and theory are presented, one on identifying problematic particulates in bilge water and the other on the effect of shearing and settling on the size of particulates found in bilge water. These could be presented as two separate papers or a single longer paper.

SECTION 2 A paper that will be presented at a special Symposium on Ecomaterials at the annual meeting of the Canadian Institute of Mining, Metallurgy and Petroleum, in Ottawa, August 2000.

SECTION 3 SEM and XPS examination of the cake layer.

SECTION 4 Silt Density Measurements.

SECTION 5 The ability of membranes to separate oil and grease.

SECTION 6 Tests to determine the influence of oil-membrane surface interactions.

SECTION 7 Cross-flow experiments.

SECTION 8 Determination of solid particulates in used oil.

SECTION 9 Treatment of bilge water before the UF membrane separator.

SECTION 10 Pilot scale trials performed with and without backpulsing. This section could be the basis for a paper on membrane fouling, Koch vs Ceramem, backpulsing vs. no backpulsing.

SECTION 11 The determination of oil and grease in water.

515557.PDF [Page: 12 of 154]

SUMMARY of CONCLUSIONS

SECTION 1 Particulate size in bilge water and the effects of shear and settling.

Paper A)

The size of particles present in bilge water were predicted from cake filtration theory and measured using the DLS (dynamic light scattering) technique. Both measurements were in excellent agreement. The results indicate that bilge water prepared from used oil contains a large amount of particulates and emulsified oil whose radii are in the range of 70 to 100 nm. Permeate flux is greatly affected by the presence of these small particles as their dimension is precisely in the range that is the most difficult to treat by cross-flow membrane filtration.

Paper B)

Experiments were performed to determine the effect of shearing on particle size. The results indicate that shearing reduced the particles from a radius of 76 -100 nm to 32 - 40 nm. In some instances, this further reduced the diffusivity of the particles. Once the bilge water was sheared, settling was not found to be a significant factor affecting the size of particles in bilge water.

SECTION 2 On the Use of Ultrafiltration Membranes in Oily Water Separators.

Particles of soot present in bilge water impose serious constraints on the treatment of this wastewater using UF membranes.

The following conclusions can be drawn from this section;

1. The permeation of water through UF membranes was found to be entirely cake/gel limited.
2. Based on flux measurements taken after one hour of filtration, two populations of particles having 3.5 and 25 nm radii were found to affect the permeate flux of UF membranes.

3. The smaller particles are likely to originate from soot while the larger particles could be soot, oil emulsions or a mixture of both.
4. A membrane having a MWCO above 10,000 Daltons should be used in this application to allow for the passage of the 3.5 nm particles which cause very high cake resistances.

SECTION 3 SEM Examination of the cake layer

The higher resolution micrographs show a large number of fine particles in the <0.2 micron size. Many small particles measuring less than 0.2 microns in diameter are present in the filter cake. This was found to be in good agreement with the DLS measurement of 89 nm radius and the filter cake calculations in Table 1.2.

The micrographs taken at lower resolutions indicate a cake layer that has de-phased on drying leaving a very open structure. It is speculated that the filter cakes contain a considerable amount of hydrophylic substances maintaining water in their structure on drying. The presence of particulates in the cake could also contribute to its resulting porous structure. The results indicate that the cake is formed from both chemically emulsified oil and particulates of soot.

XPS measurements

Metals such as iron, vanadium, molybdenum or manganese were not detected on either the GK or GH membranes tested. Carbon was the major element present on the surface of the cake. Other elements detected by XPS such as sulfur could come from the sulfates present in the bilge water while nitrogen which is present in greater quantities in the "clean" membrane than on the cake can be attributed to the Thin Film Composite membrane usually produced from polyamide. Oxygen could originate from the detergents and possibly from the hydrolyzed used oil.

SECTION 4 Silt Density Measurements

Attempts were made to determine the Silt Density Index of bilge water. After several attempts, it was deemed useless to obtain an SDI value for this wastewater as it was found to contains too many particles. The prescribed method to follow in such a case would be to pretreat the feed to reduce particulate matter before sending it to a Reverse Osmosis, Nanofiltration or Ultrafiltration membrane system.

SECTION 5 The ability of membranes to separate oil and grease.

The quality of the permeate was relatively independent of the molecular weight cut-off of the membrane. This indicated cake dominated filtration. Although the amount of permeate tested for the GH membrane is very low, the relatively large amount of oil passing through the membrane coincides quite well with the observations deduced from Figures 3.5 to 3.8 where a cake was not observed for the GH membrane and a cake was observed for all other membranes. The pore radius of the GH membrane is 2.0 nm which should have separated 40 nm particles. This suggests that some oil is dispersed at the molecular level or oil emulsions are destabilized on contact with the membrane. In the presence of a cake, free oil is scrubbed clean from solution as the feed passes through the cake. In essence. the cake enhances the separation of free oil by capturing it in its structure. This suggests that the state of the emulsified oil be it chemical or mechanical forming the cake will affect the separation process. The cake layer acted as a dynamic membrane. Further studies are required to verify the role of the cake as a dynamic membrane in removing the <2.0 nm radius oil and grease particles from the feed stream

SECTION 6 Tests to determine the influence of oil-membrane surface interactions.

In order to verify that free oil was not irreversibly coating the surface of the membrane, experiments were performed where free oil was poured directly onto the surface of the membrane prior to the permeation run. The results indicate that new oil does not readily adsorb and block membrane pores. This clearly demonstrates that new oil is not limiting

the permeability of the 30,000 Dalton MWCO membrane (which is close to the 50,000 Daltons presently used aboard HMC ships). To determine the affinity of used oil for the membrane, the test described above was repeated with used oil in the absence of pressure. After a period of 24 hours in the stir cell, 90 % of the membrane surface was free of oil and just as clean as at the beginning of the test.

These tests indicate that the membrane can recover from the de-phasing of free oil at its surface. Also that hydrophilic membrane materials do exist, such as that used in the fabrication of the QW membrane, that reduce or eliminate free oil as a cause of membrane fouling.

SECTION 7 Cross-flow experiments

All membranes were tested in a cross-flow cell operated at 1 to 1.8 m/s cross-flow velocity. These results show a substantial drop in flux for the QX membrane (70 nm pore radius) versus that of the P707 membrane (14 nm pore radius). This suggests the entrapment of the 70-100 nm (radius) particles in the QX membrane. Under these circumstances, the membrane to be used in this application should have a pore radius that is below the smaller particle radius of 40-70 nm or above the 100 nm particle radius. The pore radius of the QX membrane falls in the middle of this range, 70 nm, as calculated from the 3,500,000 Dalton MWCO or 0.01 to 0.1 microns from the Manufacturer's specifications. This lead to pore blockage in the QX membrane and a resulting flux decline.

SECTION 8 Determination of Solid Particulates in Used Oil

The amount of particulates in used oil was determined by dilution in hexane and subsequent filtration. The content of soot particles > 0.45 microns was determined to be 4.9 % by weight used oil. The filtrate was then passed through a 0.02 micron Anopore ceramic membrane and the amount of particles in the 0.02 to 0.45 micron range

determined to be 0.72 % by weight used oil. The total soot content of the used oil was determined to be 5.62 % by weight used oil.

SECTION 9 Treatment of bilge water before to the pre-filter to the UF membrane separator.

Ultrasonic treatment increased the resistance of the filter only marginally compared to the considerable increase observed with the untreated bilge water. This was attributed to the more rounded shape of 2 to 4 micron sized particles found in sonicated bilge water. These differences disappeared when the 5 micron filter was tested suggesting that sorption plays a role in the accumulation of particles within the 100 micron filter.

Treatment with the centrifugal pump caused the opposite effect where the resistance of the filter increased substantially due to treatment. This suggests that particles are aggregating on shearing in the cetrifugal pump. This also implies that excessive pumping of the bilge water before filtration will cause aggregation, enhancing the accumulation of particles in the filter media.

The results suggest the use of a filtration medium in the pre-filter that will not act as a deep bed filter. They also indicate that modules having larger lumen sizes be tested to remove the particulate retention load on the pretreatment step (dead-ended filtration) and move it to the cross-flow filtration where the micron sized particles can be removed and disposed of in the concentrate stream.

SECTION 10 Pilot scale testing.

Permeate Quality

From the pilot scale studies it was observed that permeate quality was independent of membrane operational parameters, including the membrane used, and bilge water composition. The average permeate qualities based on SPE C18 results were 24 ppm and 17 ppm, for the CERAMEM LMA and KOCH CM membranes respectively; however the

error associated with the solid phase extraction method is sufficient to neither confirm nor deny the production of an acceptable permeate quality. Based upon the conversion factor of 0.54 to convert SPE C18 extraction to hexane extractable oil and grease (see SECTION 11) these values would be 12 and 9 mg/L respectively which meet the 15 mg/L hexane extractable regulations for overboard discharge.

Fouling

An important component of system efficiency is a membrane's ability to resist fouling and to regain its initial flux after it has experienced fouling. The amount of irreversible fouling associated with the membranes was determined. This was assessed by comparing the pure water permeate flux of the membranes before and after bilge water treatment. With respect to irreversible fouling, the KOCH CM membrane proved superior to the CERAMEM LMA membrane. The KOCH CM membrane did not appear to experience any appreciable flux decline over the course of its usage. However, the CERAMEM LMA membrane experienced longer term flux decline. This was noted in both the reduction in its pure water permeate flux rate prior to and after its series of experimental runs and a continual decline, over each experimental run, in its initial bilge water flux rates. Additionally, as determined by examination of the backflushing efficiency it appears that the cake layer strongly adheres to both membranes, evidenced by the observation that the backflushing did not provide the degree of flux improvement theoretically suggested.

Backflushing

The effect of backflushing was primarily examined from its impact upon flux enhancement for the treatment of bilge water, consisting of new lubricating oil. Backflushing resulted in a marginal increase in flux capacity. Further investigation into the (theoretically predicted) benefits of backflushing revealed that the pressure and duration of the applied backflushes, used in the experimental runs, should have been sufficient to completely remove the cake layer; however, this was not observed. This

over prediction could be attributed to the oil emulsions within the cake layer adhering to the surface of the membrane.

Comparison of identical degrees of backflushing, but differing backflushing cycles – i.e. CERAMEM LMA membrane with 2.5/60 and 5/120 backflushing runs – revealed an improvement in backflushing effectiveness for the larger backflush time. This lends credence to the belief that oil may be adhering to the membrane surface as the increased backflush duration could result in increased "scouring" of oil from the membrane surface. Increasing the backflushing efficiency could be accomplished by two means, increasing the backflush pressure or increasing the duration of backflush.

Additionally, the optimization of backflushing was investigated. While the theory under predicted the efficiency of backflushing it did provide good prediction of the optimal backflushing regime, i.e. duration of backflushing per total cycle time.

Pre-Treatment

Pre-treatment, prior to membrane separations, is commonly accepted engineering practice for a number of reasons, the least of which is the prevention of system fouling by relatively large particles, by a membrane's standard. However, during the experimental runs with the KOCH CM membrane, for the treatment of used bilge water, it was shown that a pre-filter provides a significant improvement in the membrane flux where permeate flux improved after each run.

Generally over time a membrane is expected to foul, resulting in flux degradation. However, with the insertion of the pre-filter, flux improved from 165 to 250 $L/m^2/hr$, over a period of approximately 100 hours (4 experimental runs).

The filter appeared to provide a coalescence medium for free and emulsified oil, as evidenced when the filter was drained at the end of the experimental runs. The filter contained significant amount of free oil that was readily discharged from the filter.

SECTION 11 The Determination of oil and grease in water.

When using SPE techniques, the amount of oil extracted is highly dependent on the type of sorbent used in the extraction process. In a mixed mechanical/chemical emulsion the amount of oil retained by a sorbent material will depend on its affinity for free oil and its ability to destabilize the chemical emulsion. A conversion factor relating the concentration of oil as determined by a solid phase extractant to the amount of hexane extractible oil was determined for eight commercially available sorbents. The sorbent found to extract the greatest amount of oil from a mixed oil/detergent system representing bilge water in the absence of salt water was octadecyl LC-C18 (SUPELCO, Oakville, Ontario). LC-ALUMINA-B, LC-FLUOROSIL and ENVI-8 had conversion factors close to unity. This indicates that they have approximately the same extraction potential with respect to oil and grease as hexane and could be used directly to yield hexane extractable oil and grease compositions.

CONTRACT OBJECTIVES

In accordance with a Mid-Project Meeting it was agreed to modify the original scope of the research project. In order to tailor the research to the specific needs of the Canadian Navy it was agreed to examine the causes of membrane flux decline, rather than the development of a membrane based treatment system. This was decided due to the Navy's procurement of a commercial bilge water membrane based treatment system and agreement by the University of Ottawa's research team and the Navy's technical officer that membrane flux decline due to the presence of particulates would most likely be the major obstacle encountered in the successful operation of the OWS. The project was later extended to include a study of the nature of the filtration cake at the surface of the membrane and methods of treatment that would reduce difficulties related to membrane pretreatment.

P515557.PDF [Page: 21 of 154]

NOMENCLATURE

AWPPA	=	Arctic Waters Pollution Prevention Act
a_p	=	solute particle radius
C_{bulk}	=	concentration of the bulk solution
C_{cake}	=	concentration within the cake layer
CSA	=	Canada Shipping Act
DND	=	(Canadian) Department of National Defence
D	=	diffusivity co-efficient
D_{brn}	=	brownian diffusivity
D_{shear}	=	shear diffusivity
IMO	=	International Maritime Organization
V	=	flux
V(t)	=	flux at a given time
$V(t_{ss})$	=	steady state flux
V_{avg}	=	average flux over the length of the non-backflushed portion of a backflush cycle
V_{bf}	=	average flux over the length of a complete operational cycle
V_{wo}	=	membrane pure water permeate flux
K	=	mass transfer co-efficient
k	=	Boltzmann constant
MARCORDs	=	Maritime Command Orders (for the Canadian Navy)
MWCO	=	Molecular Weight Cut-Off
OWS	=	Oily Water Separator
PEG	=	Polyethylene Glycol
PEO	=	Polyethylene Oxide
PVDF	=	Polyvinylidene difluoride
P_{crit}	=	critical capillary pressure
ppm	=	parts per million
R	=	resistance
R_{foul}	=	fouling resistance

P515557.PDF [Page: 22 of 154]

R_{cake}	=	cake layer resistance
R_{mem}	=	membrane resistance
R_{total}	=	total resistance
$\hat{R}_{cake}$	=	specific cake layer resistance
r_l	=	membrane flow channel (i.e. lumen) radius
r_{oil}	=	oil droplet radius
r_{pore}	=	membrane pore radius
SPE	=	Solid Phase Extraction
T	=	temperature
TDS	=	Total Dissolved Solids
TOG	=	Total Oils and Greases
TSS	=	Total Suspended Solids
t	=	time
t_{bf}	=	time of the backflush
t_{op}	=	time of normal operation (i.e. $t_{total} - t_{bf}$)
t_{total}	=	complete operation cycle time; including both the backflush and normal operation time
t_{ss}	=	time required for the cake layer to achieve steady state
U	=	cross-flow velocity
ΔP	=	transmembrane pressure
δ	=	cake layer thickness
δ_{ss}	=	steady state cake layer thickness
θ	=	contact angle of an oil droplet to a membrane pore
σ	=	oil-water interfacial tension
ϕ	=	solute volume fraction
ϕ_b	=	solute volume fraction of the bulk solution
ϕ_{max}	=	maximum solute volume fraction (at the cake layer)
$\dot{\gamma}$	=	local shear rate
$\eta(\phi)$	=	relative viscosity

P515557.PDF [Page: 23 of 154]

$\eta(\phi_b)$	=	bulk relative viscosity
κ	=	shear induced diffusion co-efficient, a dimensionless function of particle volume
μ	=	dynamic viscosity
τ_c	=	time dependent flux decline constant
τ_w	=	wall shear stress
τ_{wo}	=	wall shear stress without a cake layer

P515557.PDF [Page: 24 of 154]

INDEX

		Page
SECTION 1	A) The identification of the most problematic particle size in the treatment of bilge water by synthetic membrane technologies. B) Effects of shear and settling on bilge water treatment by Ultrafiltration.	1
SECTION 2	On the use of Ultrafiltration Membranes in Oily Water Separators.	33
SECTION 3	SEM and XPS examination of the cake layer	51
SECTION 4	Silt Density Measurements.	68
SECTION 5	The ability of membranes to separate oil and grease.	69
SECTION 6	Tests to determine the influence of oil-membrane surface interactions	71
SECTION 7	Cross-flow experiments	73
SECTION 8	Determination of solid particulates in used oil	74
SECTION 9	Treatment of bilge water before the UF membrane separator.	75
SECTION 10	Pilot scale trials	84
SECTION 11	The determination of oil and grease in water	118

SECTION 1 Two papers having some common elements but different objectives.

A) The identification of the most problematic particle size in the treatment of bilge water by synthetic membrane technologies.

ABSTRACT

The treatment of bilge water aboard ships using membrane technologies is a challenging separation process. Bilge water is a mixture of used lubricating oils and detergents. It varies greatly in composition and strength. This wastewater contains a high amount of dissolved solids, defined as particles measuring less than 0.45 microns, which cannot be accounted for as dissolved salts alone. Bilge water is by nature difficult to treat by membrane processes.

The presence of used lubricating oils in bilge water implies that particles of soot will be present in this wastewater. It was found that excess free oil exists in bilge water and that it is a mixture containing a mechanical emulsion, a chemical emulsion and particles of soot that can act as nucleating sites for oil.

The size of particles present in bilge water were predicted from cake filtration theory and measured using dynamic light scattering (DLS) measurements. Both measurements were in excellent agreement. The results indicate that bilge water prepared from used oil contains a large amount of particulates and emulsified oil whose radii are in the range of 70 to 100 nm. Permeate flux is greatly affected by the presence of these small particles as they fall in the size range, whose combined Brownian and shear diffusivities are at a minimum and as a consequence are the most difficult particles to treat by cross-flow membrane filtration.

B) Effects of shear and settling on bilge water treatment by Ultrafiltration.

ABSTRACT

Bilge water is a mixture of used lubricating oils and detergents. It varies greatly in composition and strength. This wastewater contains a high amount of dissolved solids, defined as particles measuring less than 0.45 microns, which cannot be accounted for as dissolved salts alone. This wastewater is by nature difficult to treat by membrane processes. The present study examines the effects of shear or pumping and settling in the preparation of a synthetic bilge water mixture.

The presence of used lubricating oils in bilge water implies that particles of soot will be present in this wastewater. It was found that an excess of free oil is present in bilge water and that it is a mixture containing a mechanical emulsion, a chemical emulsion and particles of soot that can act as nucleating sites for oil. In a previous study, (refer to this from paper A)), the size of particles present in the bilge water was predicted from cake filtration theory and compared to the distribution of particles from dynamic light scattering (DLS) measurements. There was excellent agreement between these values.

The synthetic bilge water mixture was found to be greatly affected by shearing where initial particles sizes of 76 and 100 nm radius were reduced to 32 to 40 nm radius. In some instances, this further reduced the diffusivity of the particles. Once sheared, settling was not found to be a significant factor affecting particle size in the bilge water.

1.1 INTRODUCTION

The release of oily wastewaters originating from a ship's bilges is of particular environmental importance as evidenced by more stringent regulations for the discharge of bilge water to the environment. Seawater and freshwater are constantly entering a ship's bilges and must eventually be discharged. In the absence of effective onboard treatment facilities this necessitates discharge to shore based treatment facilities or barges which may or may not have treatment capabilities thus adding significantly to the cost of discharge. Bilge water is a complex and highly variable mixture of several components such as seawater, lubricating oil, greases, marine diesel fuel, hydraulic oil, detergents, metal oxides (rust particles), corrosion inhibitors, asbestos and other insulation particles, refrigerants and other wastes.

Bilge water is usually treated by settling followed with coalescence. It is first gravity separated in a parallel plate separator and coalesced in a series of hydrophobic filters to promote the agglomeration of oil droplets. In practice the ship's movement affects the efficacy of the plate separators. In several instances this method of treatment produces an effluent that does not meet the requirements for overboard discharge.

Ultrafiltration has been used for over two decades in the treatment and recycling of spent cutting oils. Cutting oils are a mixture of lubricating oils and surfactants. The use of membranes in this application is well established and commercial systems are readily available. Treating cutting oils with ultrafiltration is relatively simple as the quality of the oil/water emulsion is high and can be controlled by proper formulation. The particulates present in the cutting oil are relatively large and are easily filtered out before they reach the membrane. In an application treating bilge water, the content of the waste, its composition or strength cannot be controlled. The quality of the oil/water emulsion is poor since bilge water containing oil, phase separates to some extent. Previous studies which have characterized bilge water have shown it to contain a large amount of dissolved solids of size below 0.45 microns.

The use of ultrafiltration to treat bilge water is relatively new. The objective of this work is to determine the effects of particulates and emulsions present in bilge water on the performance of UF membranes. More specifically, to determine the size of the most problematic particles contained in bilge water and the change, if any, of these particles with time and shear history. In order to limit the amount of shear imposed on the synthetic bilge water used in this work, the experiments were performed in a stir cell which uses a magnetic stirrer to provide cross-flow at the surface of the membrane. This permits the study of bilge water subjected to a minimum amount of shear. This provides a baseline for determining the effects of pumping and settling on the bilge water. All experiments were performed with a synthetic bilge water mixture of similar composition and strength to that of bilge water found aboard HMC ship's.

1.2 GENERAL BACKGROUND

The performance of membrane processes such as Reverse Osmosis (RO), Nanofiltration (UF), Ultrafiltration (UF) and Microfiltration (MF) is greatly affected by the presence of particulates in their feed streams. The influence of natural organic matter (NOM) on permeate flux in ultrafiltration is a problem which seriously limits the use of UF and NF in the large scale treatment of municipal waters. Particulates in the order of magnitude of 0.1 micron were predicted to be a major cause of flux decline in the treatment of water containing natural organic matter (Sethi and M.R.Weisner, 1995). Waters containing particles of this size were modeled as being the most costly to treat due to the particle's very low combined Brownian and Shear diffusivities causing them to accumulate at the surface of the membrane.

Onboard ships, wastes, and in particular liquid wastes, collect in a ship's bilges. This resulting "bilge water" has a high oil content, especially bilge water produced in the main machinery spaces, due to the leakage of oils and greases from shipboard machinery. One of the earliest sources of marine pollution is the pollution of the seas by oil, with oily-water discharge regulations first being enacted by the IMO in 1959 (IMO, 1999).

Subsequently, due to increasing environmental awareness, the regulations have become more stringent.

In order to effectively treat bilge water, a process must be capable of addressing the different oil compositions in bilge water. Oil is present in bilge water as either free or emulsified oil. The emulsified oil can be further divided into the two categories of mechanical and chemical emulsions. Mechanical emulsions are those created by the physical mixing of oil and water. This can occur due to the movement in a ship's bilge and tanks, and the pumping of bilge water. Chemical emulsions are the result of the addition of detergents and surfactants to the bilge water. These detergents and surfactants are necessary for other shipborne aspects (i.e. ships' husbandry, fire fighting, boiler water treatment, etc...) and ultimately accumulate in a ship's bilge.

For an Oily Water Separator (OWS) to be effective in a marine environment it not only has to meet environmental regulations, but also must address shipborne concerns. These additional criteria can be summarized as follows:

a. substantial volumetric reductions are required due to the limited physical space to hold the membrane concentrate;
b. system size, again due to the limited physical space; and
c. system automation; as an OWS is an ancillary system direct operator supervision should be limited.

1.2.1 Oil Discharge Environmental Regulations

The environmental regulations pertaining to oil pollution for the Canadian marine sector stem from the following jurisdictions: international, the International Maritime Organization (IMO), and national, the Canada Shipping Act (CSA) and the Arctic Waters Pollution Prevention Act (AWPPA). The Canadian Navy also has their own regulations, as detailed in Maritime Command Orders (MARCORDs). While these regulations are rather complex, their synopsis is as follows (CSA, 1999 and AWPPA, 1999):

a. within Canadian inland waters and various fishing zones (e.g. Grand Banks) – undiluted effluent discharged overboard cannot exceed 5 ppm of oil;

b. within 12 nautical miles of Canadian coastline – undiluted effluent discharge overboard cannot exceed 15 ppm of oil;

c. beyond 12 nautical miles off land – undiluted effluent discharged overboard cannot exceed 100 ppm of oil; and

d. in the Arctic Ocean (i.e. beyond 60° of latitude), no bilge water discharge, unless it is unavoidable and essential to a ship's operation.

While all navies are under no legal obligation to adhere to the CSA, AWPPA or IMO regulations (CSA, 1999) the Canadian Navy has imposed its own restrictions (through MARCORDs) upon the discharge of bilge water (DND, 1999):

a. within 12 nautical miles of land - no effluent shall be discharged;

b. within 200 nautical miles of land – effluent discharge overboard cannot exceed 15 ppm oil; and

c. all Canadian ships will comply with the environmental regulations of other nations, as applicable.

Therefore in order for Canadian Navy ships to discharge bilge water overboard they must possess an OWS system capable of reducing the oil content of bilge water to at least 15 ppm oil. Within Canadian waters, excluding the arctic, an OWS system must be capable of reducing bilge water oil content to 5 ppm oil. Assuming that transits within Canadian waters are fairly short then it would be possible to not discharge bilge water during this interval. Therefore, the most pressing requirement would be to achieve the international standard of no more than 15 ppm oil in effluent discharge, but it would be highly preferable to also achieve an effluent discharge of no more than 5 ppm oil.

1.2.2 Physio-Chemical Nature of Bilge Water

The treatment of bilge water is a technically demanding challenge due to the fact that bilge water is not merely oily water. It is contaminated with a wide variety of substances, plus its oil component is often, but not always, emulsified (Marine Engineering Review, 1997). Additionally, it is important to remember that "the composition of bilge water is neither stable nor predictable" (Marine Engineering Review, 1997).

To properly consider the treatment of bilge water it is necessary to examine the impacts of the properties of bilge water. Some of these characteristics include composition, oil emulsification, pH, and temperature. The following bilge water characteristics represent an average sampling. At any given time the composition of bilge water can and does vary widely from this average. Variations from the average composition will pose unique problems to an OWS system and therefore it must be designed to accommodate such extremes. The largest variable is likely the oil in bilge water, both in terms of the oils present and their quantity. For example, the lube oil change of a diesel engine and/or diesel electrical generator can result in substantial influxes of used oil into the bilge in very short periods of time.

Composition

Due to the wide variety of components that make up bilge water plus the fact that its composition will vary from ship to ship and mission to mission it is virtually impossible to accurately determine the composition of bilge water at any given time. The primary components of bilge water are sea (salt) and fresh water, in approximately equal proportions. Bilge water contaminants vary widely, with some of the potential contaminants being: diesel fuel, lubricants and greases, solvents, bilge cleaners, refrigerants, paints, boiler compound, food products, bacteria, cigarette butts, and various solid particles (rust, carbon, scale, pipe insulation).

A study conducted on behalf of the Canadian Navy described bilge water composition in the following categories (Resera, 1995):

a. Total Oils and Greases (TOG);
b. Total Suspended Solids (TSS). TSS were defined as solids larger than 0.45 microns in diameter;
c. Total Dissolved Solids (TDS). TDS were defined as solids smaller than 0.45 microns in diameter;
d. detergents; and
e. sea and fresh water.

The average composition of bilge water was determined to be (Resera, 1995):

a. TOG = 1,284 mg/L;
b. TSS = 502 mg/L;
c. TDS = 17,735 mg/L; and
d. water (50% sea, 50% fresh) = remainder = 97.55%.

Examination of each of these parameters provides some insight into the make up and variability of bilge water.

Total Oils and Grease (TOG). While the average TOG value was found to be approximately 1,300 mg/L it varied from 15 to 7,000 mg/L, based upon a study examining 37 bilge water samples (Resera, 1995). Additionally, TOG provides a somewhat distorted view of the oil content of bilge water as this will include non-harmful oils and greases, such as vegetable oils and animal fats which originate from a ship's galley. Accordingly, it was found that petroleum based hydrocarbons accounted for approximately 85% of the TOG value (Resera, 1995). The primary types of oils found in bilge water are naval distillate (i.e. marine diesel fuel), naval diesel engine lubricating oil and hydraulic oil (DND, 1996). While the quantity of petroleum hydrocarbons in bilge water is useful, another useful parameter would be an indication of the amount of free and emulsified oil, as differing types of separation processes are more effective for the removal of free or emulsified oil.

Linked to the degree of emulsified oils present in bilge water is the quantity of detergents found in bilge water. Detergents are very much a component of bilge water as they are used onboard ships for a variety of purposes. The quantity of detergents present will have a direct link to the amount of emulsified oils present in solution. The Canadian Navy has estimated the quantity of detergents to be approximately 500 mg/L (DND, 1996). Additionally, while numerous types of detergents are commercially available the Navy has attempted to limit the number used onboard ships. The primary types of detergents found onboard Canadian Navy vessels are CLEANBREAK (a petroleum based, commercially available, detergent), ZOK-27 (a water based, commercially available, detergent) and a corrosion removing compound (containing phosphoric and oxalic acids). (DND, 1996)

Total Suspended Solids (TSS). As with TOG the quantity of TSS also varied significantly; ranging from 0 to 2,750 mg/L, with an average of approximately 500 mg/L.

Total Dissolved Solids (TDS). The average value of the TDS suggests that it is essentially the salts found in sea water, since sea water has an average salt content of approximately 35,000 mg/L and sea water comprises 50% of the water component of bilge water. However, the Canadian Navy study found that TDS ranged from 700 to 32,050 mg/L, with the average content being approximately 17,700 mg/L (Resera, 1995). The upper end of this range, 32,050 mg/L, would suggest that the TDS are comprised of more than just sea salts. Examples of other possible TDS sources may be rust particles and carbonaceous sediment found in the lubricating oil from diesel engines. This upper range also indicates that a substancial amount of sub 0.45 micron sized particles can exist in bilge water.

1.3 Defining bilge water

In practice, there exists considerable ship to ship and time variations in the composition and strength of bilge water. Performing membrane permeation tests on a sample of bilge water from one ship does not necessarily provide treatability estimates

for all ships in the Canadian Navy. The use of synthetic mixtures, provides an insight into the effect of various components on membrane performance.

Lubricating oil found in bilge water originates from the crankcase of diesel engines aboard ships. In a preliminary test, the ability of UF membranes to separate a bilge water mixture containing either new or used oil was studied. The bilge water mixture was mixed, then treated in a stir cell with a membrane having a molecular weight cutoff (MWCO) of 20,000 Daltons. The permeate flux for the new and used oil vs.time for a trans-membrane pressure of 3.36 bar (50 psi) are plotted in Figure 1.1.

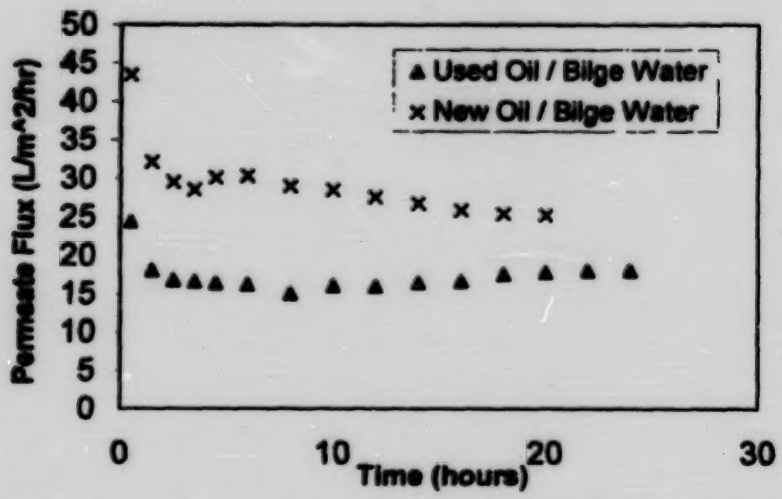

Figure 1.1. Plot of permeate flux vs time for a 20,000 Dalton MWCO membrane.

As seen in Figure 1.1, a very steep initial decline in permeate flux occurs for the test using used oil. Membrane flux using used oil remained nearly half of that of new oil over the first 15 hours of the test and remained lower over the next 9 hours of the membrane test. As used oil is found in bilge water, it was used in all further tests.

1.4 THEORY

The suitability of a membrane for a particular application is determined by its ability to separate solute, maintain a targeted flux, and withstand repeated cleaning cycles. The factors affecting membrane performance are its ability to separate solutes, its resistance to permeation and the resistance of any gel or cake player accumulating on the surface of the membrane to permeate flow, the transmembrane pressure, the cross low velocity in the feed channel and the viscosity of the permeate.

In the absence of solutes and particulates, flow through the membrane will be governed by the resistance of the membrane. This is commonly referred to as a membrane's "pure water permeate" flux (V_{wo}) known to be a function of operating (transmembrane) pressure (ΔP), viscosity of water (μ_o) and the membrane resistance (R_m) to permeation. Permeation of pure water through a clean membrane, is expressed as (Eykamp, 1995):

$$V_{wo} = \frac{\Delta P}{\mu_o R_m} \tag{1}$$

However in the treatment of watewaters, particles will be present in solution and will accumulate on the surface of a UF membrane. For liquid separation, membrane flux can be expressed in terms of resistances as follows:

$$V_w = \frac{\Delta P}{\mu_o (R_m + \delta_{st} \hat{R}_{cake})} = \frac{V_{wo} R_m}{(R_m + \delta_{st} \hat{R}_{cake})} \tag{2}$$

Where, V_{wo} is the permeate flux, $\hat{R}_{cake}$ is the specific resistance of the cake and δ_{st} is the stagnant cake layer thickness. The total system resistance $(R_m + \delta_{st} \hat{R}_{cake})$ is the combined resistances of the membrane and cake.

Solute particles accumulating at the surface of the membrane as fluid passes through the membrane create a local concentration gradient. This "polarization" of solute, termed concentration polarization is a natural consequence of membrane filtration, it cannot be avoided and must be minimized.

In traditional dead-ended filtration, particles readily accumulate as a cake at the surface of the filter. The cake can be removed by reversing the direction of permeate flow (backflushing). In cross-flow filtration the feed solution is circulated tangentially across the surface of the membrane sweeping solute particles away from the surface of the membrane. However, this cross-flow action is limited by the existence of a boundary layer at the surface of the membrane. Particles or solute in this boundary layer must back diffuse into the bulk solution in order to be swept away by the feed solution. The accumulation of particles or solute in the boundary layer will depend on the thickness of the boundary layer and the diffusivity of the particle or solute.

In both dead-ended and cross-flow filtration, the cake layer grows causing a reduction in permeate flux. The thickness of the cake layer reaches a steady state value when the flow of solute or particles towards the cake layer equals the diffusion of solute or particles away from the cake layer. A boundary layer is present above the cake layer where the solute concentration is in transition from the bulk to the greater cake layer concentration.

For membranes with relatively large pores the flux will be high and therefore the effect of concentration polarization will be important. For membranes with relatively small pores membrane flux will be low and therefore the degree of concentration polarization will also be low (Mulder, 1995). However, the mass transfer co-efficient is strongly influenced by the operational (hydrodynamic) characteristics of the system. Specifically, the mass transfer co-efficient is defined as the ratio of the diffusion co-efficient (D) and the cake layer thickness (δ) and can be expressed as :

$$K = \frac{D}{\delta} \tag{3}$$

1.4.1 Cake Layer Resistance

As described above, the cake layer is the result of concentration polarization phenomena. It is a thin film, lying directly on the membrane surface. This cake layer provides additional filtration properties and its resistance can be described as (Davis, 1992):

$$R_{cake} = \delta_{st}\ \hat{R}_{cake} \tag{4}$$

Several means of evaluating the specific cake layer resistance exist, one of which is estimation by means of the Blake-Kozeny equation (Davis, 1992):

$$\hat{R}_{cake} = \frac{37.5\phi_{max}^2}{a_p^2(1-\phi_{max})^3} \tag{5}$$

Where ϕ_{max} is the maximum solute volume fraction of the cake layer and a_p is the radius of the solute particle. The cake layer thickness can be determined from the maximum solution volume fraction and the solute particle size. For rigid spheres, the maximum solute volume fraction is known to be 0.58 (Sethi and Wiesner, 1995) therefore the only remaining variable needed to determine the specific cake layer resistance is the solute particle radius.

If a solution, such as bilge water, is composed of a range of different particle sizes, the particle most likely to be found in the cake layer will be the one having the lowest diffusivity. The total diffusivity of a particle in solution is the sum of its Brownian (D_{brn}) and Shear (D_{shear}) diffusivities, defined as (Davis, 1992, Sethi and Wiesner, 1995):

$$D_{brn} = \frac{kT}{6\pi\mu a_p} \tag{6}$$

$$D_{shear} = \dot{\gamma}\ a_p^2\ (0.33\phi^2(1+0.5e^{8.8\phi})) \tag{7}$$

Where k is Boltzmann's constant, T is temperature and $\dot{\gamma}$ is the local shear rate. The local shear rate is the velocity gradient within the cake layer and can be expressed as (Davis, 1992):

$$\dot{\gamma} = \frac{\tau_w}{\mu\eta(\phi)} \tag{8}$$

Where τ_w is the wall shear stress and $\eta(\phi)$ is the relative viscosity.

1.4.2 Comparing the total diffusivity of particles separated in a small tube UF and a stir cell.

In a stir cell, the shear rate will vary radially, increasing as a function of the radial position away from the center of the stirrer. However, for representative purposes, a radius which divides area of the membrane in half can be used for illustrative purposes. Figure 1.2 illustrates the diffusivity of solute particles as a function of particle size at a radial distance of 0.025 m in a 0.07 m diameter stir cell with a 0.05 m long magnetic stirrer rotating at 900 rpm, 3 mm above the surface of the membrane.

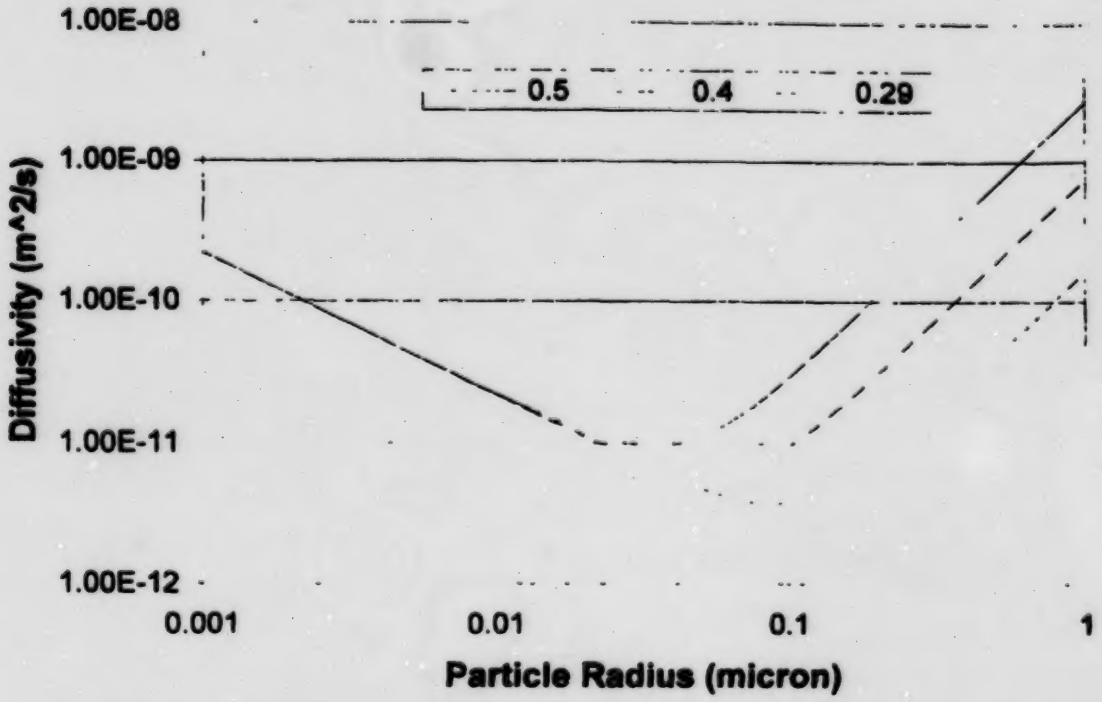

Figure 1.2. Plot of the diffusivity vs. particle radius at a radial distance of 0.025 (m) from the center of the membrane surface in a stir cell for particle volume fractions within the cake layer of $\phi = 0.29$, 0.4 and 0.5.

For flow in a lumen of circular cross section the wall shear stress and the relative viscosity are defined as (Sethi and Wiesner, 1995):

$$\tau_w = \frac{4U\mu\eta(\phi_b)}{r_l - \delta} = \frac{\tau_{w,0} r_l^3}{(r_l - \delta)^3} \tag{9}$$

$$\eta(\phi) = \left(1 + \frac{1.5\phi}{1 - \frac{\phi}{0.58}}\right)^2 \tag{10}$$

Where U is the cross-flow velocity and r_l is the radius of the membrane flow channel.

A system's variables that can alter the cake layer's diffusivity are the cross-flow velocity and solute concentration (i.e. the concentration of oil in bilge water). Figure 1.3 is a plot of the total diffusivity of a particle versus particle size, for flow in a 1.143 mm diameter lumen, a solute volume fraction within the cake layer of 0.29, a cross-flow velocity of 0.9 m/s and an a particulate concentration of 250 mg/L.

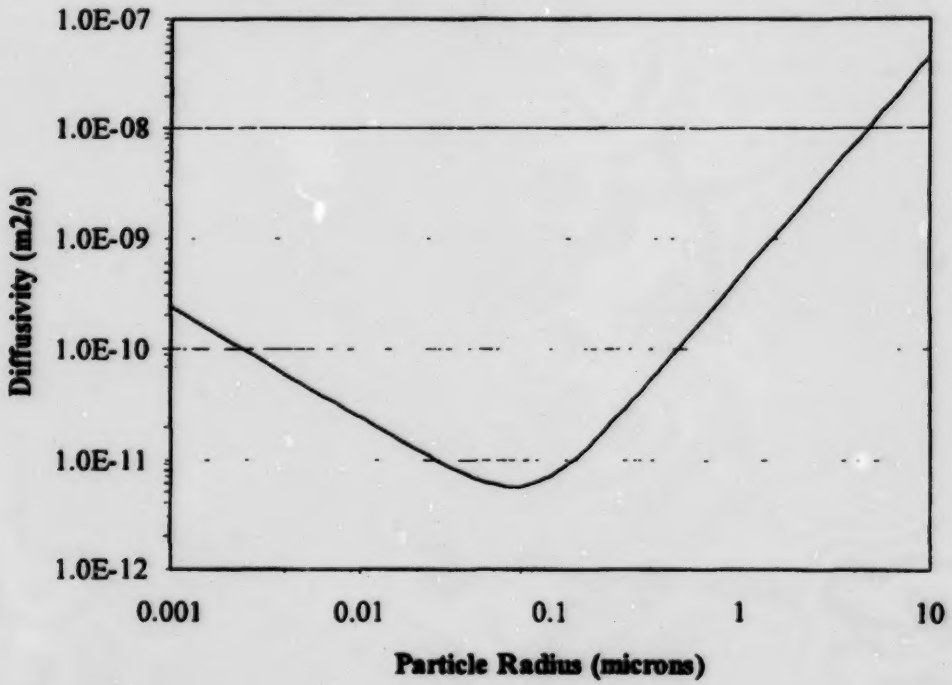

Figure 1.3. Effect of Particle Size on Cake Layer Diffusivity

As seen in Figure 1.3 the critical particle radius, associated with the minimum diffusivity, is below 0.1 micron – approximately 0.065 micron. While it is impossible to identify a precise critical solute particle size it is reasonable to expect that the range of

critical solute particle sizes, for MF and UF will be approximately 0.01 to 0.1 microns for both a stir cell and small tube modules.

1.4.3 Time Dependent Permeate Flux

Another critical parameter that must be examined is operating time. In cake filtration, flux will decline as the cake, or gel, layer builds up on the surface of the membrane. However, as previously mentioned, the flux decline associated with the cake layer resistance will stop once the cake layer achieves its steady state, or equilibrium conditions (Davis, 1992).

While the effects of fouling, upon membrane resistance, are difficult to quantify the effects of the cake layer on permeate flux are relatively predictable. Until the cake layer achieves its steady state conditions the flux can be expressed as a function of the pure water permeate flux and the associated time decay. This can be generically expressed as (Mulder, 1995):

$$V_w(t) \propto V_{wo}\ t^m \tag{11}$$

Where *Vwo* is the pure water permeate flux, t is the length of time that the system has been in operation and t^m is the decay in pure water flux associated with the time of system operation.

The value of m is always less than zero and is a function of the cross-flow velocity (Mulder, 1995). The greater the cross-flow velocity the more the value of m will approach zero – i.e. for an infinite cross-flow velocity the flux at any time will always be the pure water permeate flux. This assumption is valid provided the particles can back-diffuse to wards the bulk solution. From a fluid dynamics perspective, increasing cross-flow reduces the thickness of the boundary layer of the membrane. The mass transfer coefficient which affects the concentration of particles at the surface of the membrane will only be reduced if the diffusivity of the particle is appreciable. Figures 2 and 3

indicate that problematic particles can have a diffusivity two orders of magnitude lower than that of sodium chloride (1.61×10^{-9} m^2/s). In practice, energy and physical considerations will limit the operating cross-flow to a point that the presence of problematic particles in feed waters will determine membrane flux.

A more detailed time dependent flux model has been proposed by Davis, 1992 where the initial stages of the filtration process are assumed to resemble dead ended filtration. This assumption can be valid in cases where particles with low diffusivities are present in the solution. These particles with low diffusivities are expected to preferentially accumulate in the cake. It is proposed to use this technique to determine the size of solutes in the bilge water which most adversely affect filtration.

An explicit solution for permeate flux can be derived from a mass balance at the edge of a growing cake layer in a dead ended filtration.

$$\left(V_w(t) + \frac{d\delta_{st}}{dt}\right)\phi_b = \phi_{\max}\frac{d\delta_{st}}{dt} \tag{12}$$

Rearranging and solving the differential equation;

$$\frac{1}{2}\delta_{st}^2\hat{R}_{cake} + \delta_{st}R_m - \left(V_{wo}R_m\frac{\phi_b}{(\phi_{\max} - \phi_b)}\right)t = 0 \tag{13}$$

The solution has two roots, the positive one giving being;

$$\delta_{st}(t) = \frac{1}{2}\left[\frac{-2R_m + 2\sqrt{R_m^2 + 2\hat{R}_{cake}\,t\left(V_{wo}R_m\frac{\phi_b}{(\phi_{\max} - \phi_b)}\right)}}{\hat{R}_{cake}}\right] \tag{14}$$

Rearranging gives;

$$\delta_{st}(t) = \frac{\left(1 + \frac{2t}{\tau_c}\right)^{1/2} - R_m}{\hat{R}_{cake}} \tag{15}$$

Where τ_c is the time constant associated with membrane flux decline, which is defined as (Davis, 1992):

$$\tau_c = \frac{R_m(\phi_{max} - \phi_b)}{V_{wo}\ \hat{R}_{cake}\ \phi_b} \tag{16}$$

Where ϕ_{max} and ϕ_b are the maximum solute volume fraction, within the cake layer, and the bulk solute volume fraction, respectively.

When the cake is developing, the effects of shear on the cake is small and can be neglected over short times such that cross-flow filtration theory can be approximated by dead ended filtration theory (Davis, 1992). The approximate time to reach steady state (t_{ss}) is determined by substituting the experimentally determined steady state value of flux $V_w(t_{ss})$ into the equations above giving;

$$t_{ss} = \frac{\tau_c}{2}\left\{\left[\frac{V_{wo}}{V_w(t_{ss})}\right]^2 - 1\right\} \tag{17}$$

Values of t_{ss} were determined for all membranes and ranged from 16 to 48 hours. In order to eliminate experimental variations occurring in flux measurements, a 24 hour period was used in determining fitted values in this work.

1.5 EXPERIMENTAL METHOD

The objective of the present study was to examine the effects of shear and settling on a synthetic bilge water mixture. The following mixture was used in this study:

a. TOG = 2000 ppm. Composed of 50% naval distillate, 40% used naval diesel engine lubricating oil and 10% naval hydraulic oil;

b. Detergents = 500 ppm. Composed of 90% Canadian Navy standard oil and grease detergent (CLEANBREAK), and 10% Canadian Navy standard corrosion removal compound (OSTREM Rust Stain Remover); and

c. Water = remaining 99.7%. Composed of a 50/50 mixture of fresh and sea water.

The composition of this cocktail is modeled on a mixture identified by the Canadian Navy as representing bilge water (DND, 1996). The modified synthetic mixture contained used lubricating oil as opposed to new oil. Used lubricating oil contains a considerable amount of soot that is imbibed with oil. This particulate loaded with oil was thought to be of greater challenge to the membrane than the addition of carbon black and other particles as it is very difficult to reconstitute dispersions of nanometer sized particles from dry solids.

Various commercial flat sheet membranes were tested in a 0.07 m diameter stir cell operated at 900 rpm, 345 kPa (50 psig) and 25.0 °C controlled to +/- 0.1 °C. Permeate flux was determined with an autosampler. The membranes were obtained from Koch Membranes (Ann Arbor, Michigan, USA) and OSMONICS (Minnetonka, Minnesota, USA). In most cases some details, such as the material forming the selective layer, was not available. The "G" series membranes produced by Osmonics were of the thin film composite type. The M100 and P707 membranes produced by Koch Membranes were made from polyvinylidine difluoride (PVDF). Table 1.1 below lists the membrane identification, its estimated pore size based on a separation of 90% at its MWCO and the pure water permeability V_{wo}.

Membrane selectivity was not always expressed in the same manner by the manufacturers, that is, most of the membranes had their selectivity expressed in terms of MWCO (molecular weight cut-off), others were given in terms of pore radius in nanometers. The correlation between MWCO and pore radius is dependent upon the polymer used to determine the MWCO. For polyethylene glycol (PEG) and polyethylene oxide (PEO) the correlation between MWCO and solute size (Tremblay, 1992) was used to determine pore radius.

Table 1.1 – Membrane pore radius, pure water permeate flux for the membranes tested in this work.

Membrane Name	MWCO (Daltons)	pore radius (nm)	PWP Flux at 345 KPa ($L/m^2/h$)
GH	2,500	2.0	6.15
GK	3,500	2.2	33.1
GM	8,000	3.3	54.2
GN	10,000	3.7	105
M100	20,000	5.2	217
QW	30,000	6.4	207
P707	150,000	14	329
QX	3,600,000	70	439

In a first set of runs synthetic bilge water was prepared in a 4 liter bottle and mixed using a magnetic stirrer. This set of experiments is labeled "no pumping". In a second and third set of experiments, 100 L of synthetic bilge water mixture was prepared in a V bottom tank and mixed with a centrifugal pump for one half hour before settling for one half hour and 24 hours. These sets are termed "one half hour" and "24 hour" settling runs.

1.6 RESULTS AND DISCUSSION

The initial membrane resistance was identified from pure water permeate runs. The permeate flux *Vw* was measured for these membranes as reported in Table 1.1 and the experimental cake resistance was determined from Equations 1 and 2. In SECTION 2 of this report it will be shown that for fresh bilge water (no pumping or circulation) there existed a discontinuity in a plot of the gel resistance vs MWCO of the membranes tested. This drop occurs between the 8 and 10 kDalton membranes. The drop was attributed to small particles measuring between 3.3 and 3.7 nm retained by the 8 kDalton membrane but not the 10 kDalton membrane. In this work, for the GH, GK and GM membranes the size of the solute particle a_p was fixed at 3.5 nm. This size corresponds to the average between 3.3 nm for the GK and 3.7 nm for the GM membranes. The concentration of these particles was determined from a least squares fit of all the data for the entire 24 hour run, of the cake resistance calculated from Equations 15 and 4 to the experimentally determined values found using Equations 1 and 2.

For the membranes having larger MWCO values, GN, M100, QW, P707 and QX, the particle radius a_p was determined by first setting the concentration of the particles in the bulk solution and performing a least squares fit of the cake resistance calculated from Equations 15 and 4 to the experimentally determined values found using Equations 1 and 2. The sum of squares of residuals between the predicted and calculated cake resistances was minimized by varying the particle radius a_p.

The bulk concentration of particles was estimated from hexane extractions where 45 % of the hydraulic oil fraction was determined as free oil. This led to a particulate concentration (including detergents) of 2100 mg/L. These results are included in Table 1.2 below.

Table 1.2. Membrane pore radius, large particle radius and small (3.5 nm) particle concentration based on a bulk concentration of large particles of 2100 mg/L.

Membrane	MWCO	Pore Radius	Fresh bilge water no pumping		Pump half hour then settle for ½ hour		Pump half hour then settle for 24 hours	
	(k Daltons)	(nm)	Large particle radius (nm)	Small (3.5 nm) particle Conc (mg/L)	Large particle radius (nm)	Small (3.5 nm) particle Conc (mg/L)	Large particle radius (nm)	Small (3.5 nm) particle Conc (mg/L)
GH	2.5	2.0	-	42.4	-		-	39.2
GK	3.5	2.2	-	67.3	-	30.9	-	29.4
GM	8.0	3.3	-	69.5	-	24.5	-	27.8
GN	10.0	3.7	59.4	-	32.4	-	76.3*	-
M100	20.0	5.2	69.7	-				-
QW	30.0	6.4			41.1	-	44.5	-
P707	150.0	14	97.4	-			40.7	-
QX	3,600.0	70	49.1	-			41.5	-

*First run on the synthetic bilge water used in the 24 hour runs.

The experimental and calculated fluxes were plotted in Figures 1.4 to 1.10 for all 24 hour settled bilge water runs as listed in Table 1.2. In most cases, the theory provides an excellent fit to the experimental measurements. The time dependent nature of the permeate flux indicates that membrane transport is dominated by cake filtration. The importance of cake filtration is further illustrated by the observation that all membrane fluxes leveled off at nearly the same values (with the exception of the GH coupon that has a very high membrane resistance).

Fresh bilge water had twice as many 3.5 nm particles than bilge water prepared by pumping. This indicates a certain degree aggregation of the smaller particles into larger ones or the scrubbing of free oil. For the larger particles, their size decreased on shearing. In all cases, their size fell well within the range of minimum diffusivity as seen in Figure 1.2.

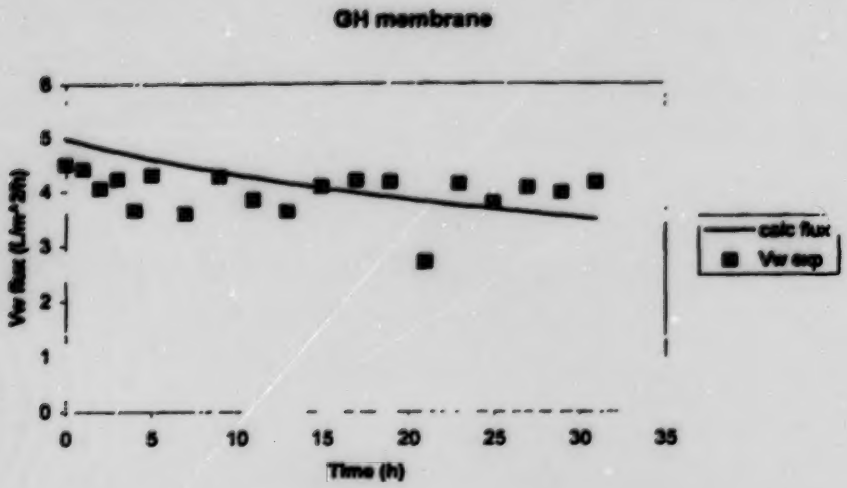

Figure 1.4. Plot of permeate flux vs time for GH membrane, 24 hour settling.

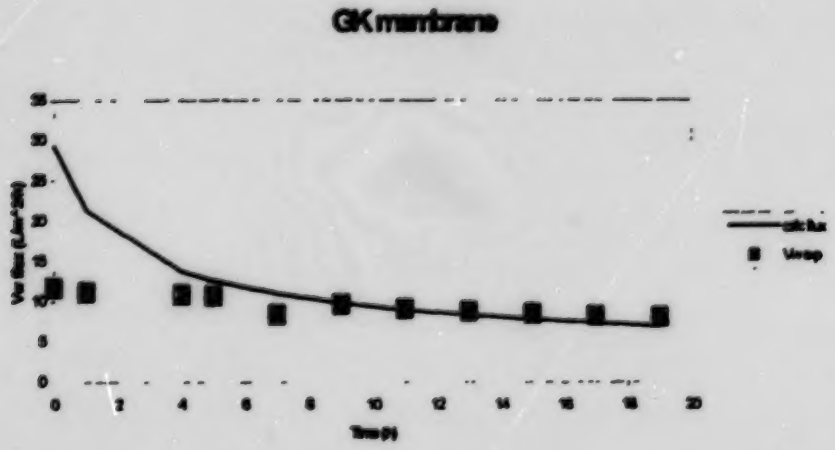

Figure 1.5. Plot of permeate flux vs time for GK membrane, 24 hour settling.

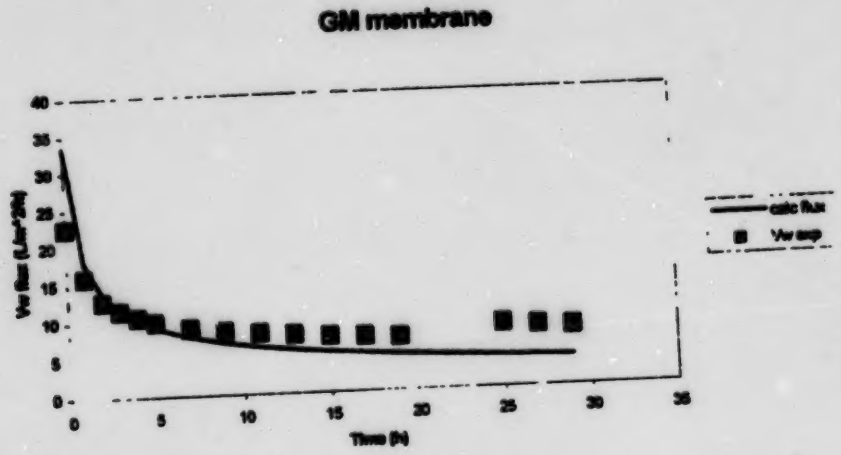

Figure 1.6. Plot of permeate flux vs time for GM membrane, 24 hour settling.

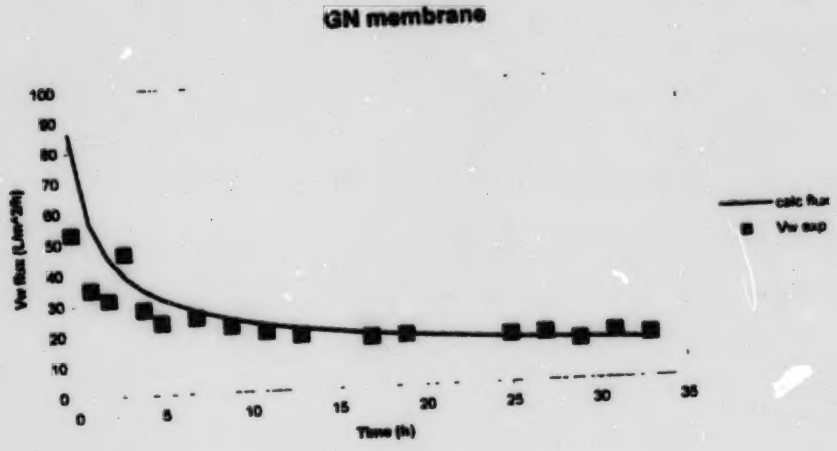

Figure 1.7. Plot of permeate flux vs time for GN membrane, 24 hour settling.

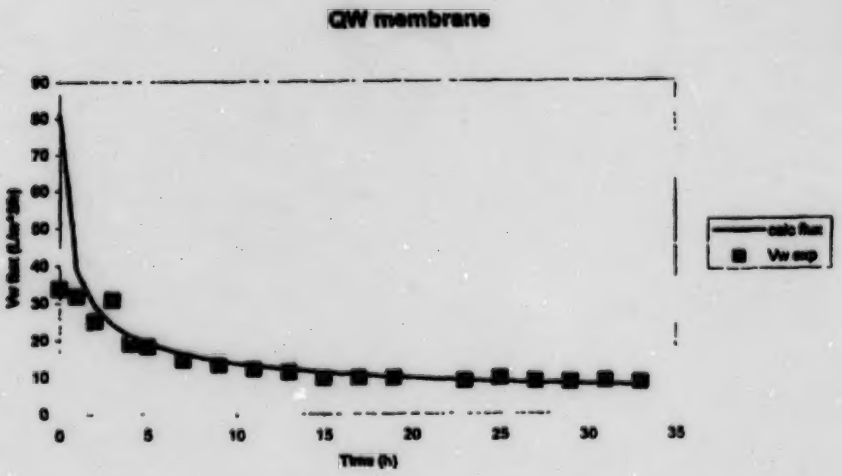

Figure 1.8. Plot of permeate flux vs time for QW membrane, 24 hour settling.

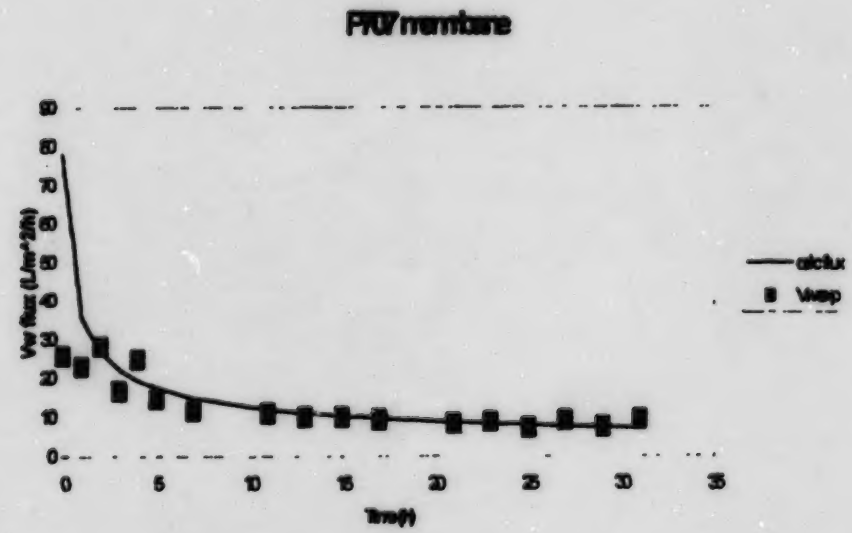

Figure 1.9. Plot of permeate flux vs time for P707 membrane, 24 hour settling.

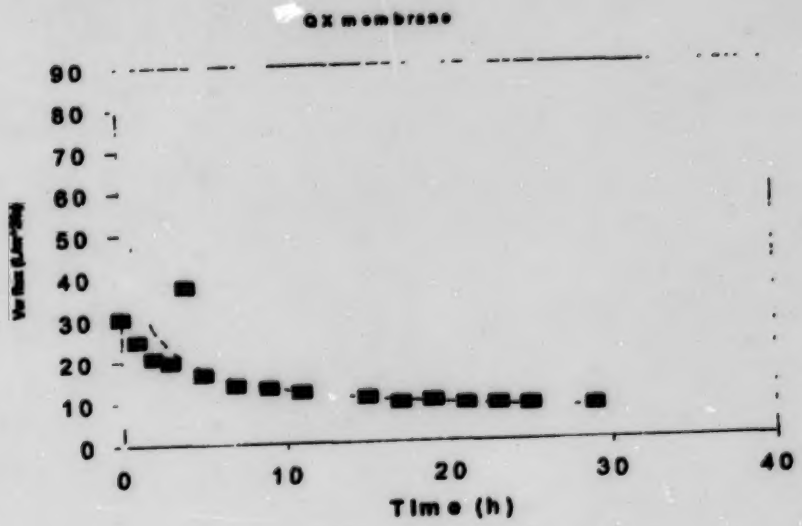

Figure 1.10 Plot of permeate flux vs time for QX membrane, 24 hour settling.

Dynamic Light scattering (DLS) measurements were performed on bilge water prepared from new oil Figure 1.11 and used oil Figure 1.12. The oil samples were not mixed in a pump prior to analysis. The results obtained from new oil show only one distribution around 0.65 microns radius which is outside the problematic low diffusion range. This explains why bilge water prepared using new oil is easily treated. The DLS results for bilge water made from used oil indicate the presence of a substantial amount of particles ranging from 70 to 100 nm with a mode of 89 nm radius. A second population of particles measured 1.34 microns which is out of the problematic range as seen in Figure 1.2. The larger size particles coincide quite well with the size of mechanical emulsions. These larger particles would have been taken into account in our analysis as hexane extractable oil and grease. They are also within the size of the larger soot particles, approx. 4.4 micron diameter that would have passed through the 5 micron nominal oil filter present in the diesel engine generating the waste oil

The values calculated from the filtration experiments on freshly prepared bilge water are in excellent agreement with these measurements. This indicates that the 70 to 100 nm sized particles are formed by reasonably stable soot and chemical emulsions and that the emulsions are not phase separating at the surface of the membrane. Irrespective of the mode of preparation, a particulate fraction that is not hexane soluble will lie in the problematic range for UF membrane separation. This indicates that bilge water separation using cross-flow membrane technologies, in the absence of any pretreatment to remove these particles will always be very challenging.

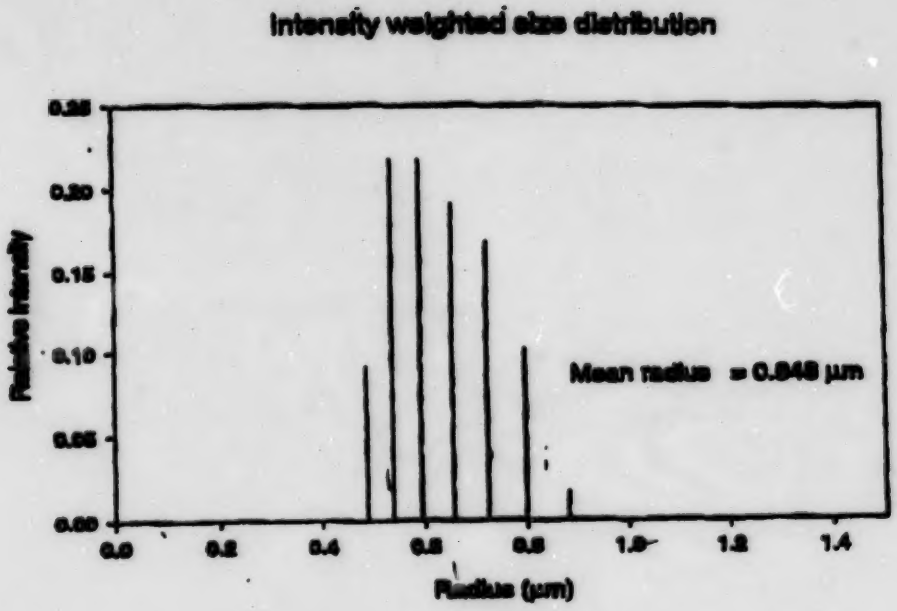

Figure 1.4 Particle size distribution for new oil.

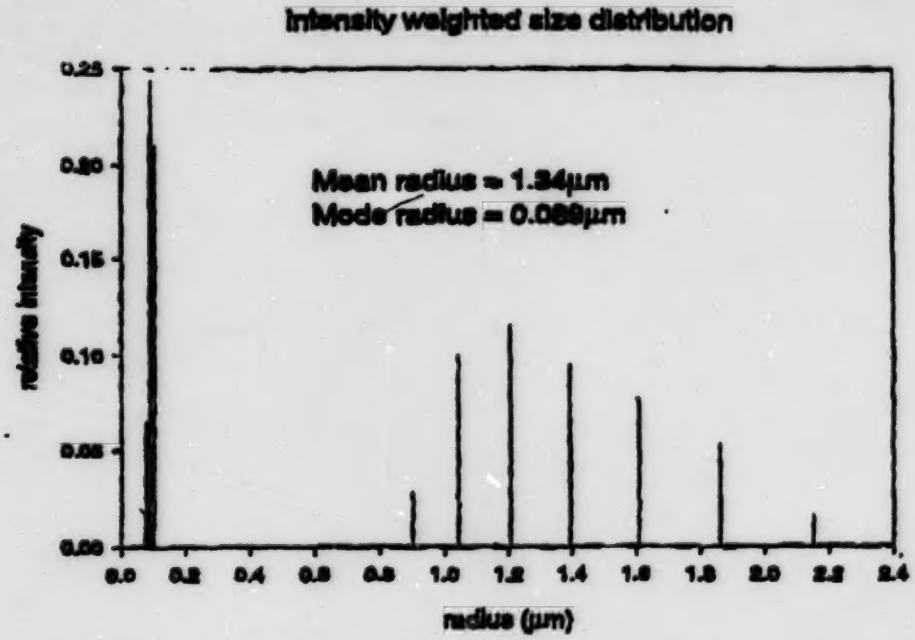

Figure 1.5 Particle size distribution for used oil. Peaks for the smaller radii are at 0.07, 0.089 and 0.1 microns.

Particulates in used oil

Used lubricating oils originating from internal combustion engines contain particles of soot formed during the combustion process. The initial size of these soot particles depends on the conditions existing in the combustion chamber at the time they were formed. Their size is difficult to estimate but carbon black particles are commercially available with average particle sizes ranging from 8 to 100 nm and a specific gravity of 1.7 to 1.9 (Columbian Chem. Co., 1997). Once formed, the carbon black particles can aggregate into larger units measuring several microns. The oil filter in a diesel engine will limit the size of soot particles present in used oil. Most oil filters in diesel engines have a nominal rating of 5 to 8 microns with an absolute cutoff of 24 microns.

Under normal operation, the larger openings in an engine's oil filter will have greater amounts of oil flowing through them than the smaller openings. Soot particles will tend to bridge in these channels and decrease the size of the openings, improving the filter's rating. This is verified by the observation of used oil under an optical microscope where the largest particle observed measured five microns. Soot particles were observed from 5 microns down to sizes well beyond the resolution of the optical microscope as evidenced by a uniform gray background in the entire field of view of the microscope.

1.7 Conclusions

Paper A)

The size of particles present in bilge water were predicted from cake filtration theory and measured using the DLS (dynamic light scattering) technique. Both measurements were in excellent agreement. The results indicate that bilge water prepared from used oil contains a large amount of particulates and emulsified oil whose radii are in the range of 70 to 100 nm. Permeate flux is greatly affected by the presence of these small particles as their dimension is precisely in the range that is the most difficult to treat by cross-flow membrane filtration.

Paper B)

Experiments were performed to determine the effect of shearing on particle size. The results indicate that shearing reduced the particles from a radius of 76 -100 nm to 32 - 40 nm. In some instances, this further reduced the diffusivity of the particles. Once the bilge water was sheared, settling was not found to be a significant factor affecting the size of particles in bilge water.

SECTION 2

Paper to be presented at the Ecomaterials Symposium of the CMI meeting

On the Use of Ultrafiltration Membranes in Oily Water Separators

ABSTRACT

Synthetic membranes are ideally suited to address the requirements of clean, sustainable processes. Ultrafiltration (UF) membranes are nanoporous materials produced from ceramic, polymeric or metallic substrates. The size of their nanopores affects the ability of the membrane to retain macromolecules, colloids, sub-micron particles and oil emulsions.

This paper reports the results of some laboratory studies on the use of UF membranes for oily water purification from ships bilges. Upper and lower bounds on membrane pore size were found to exist for the best operation of the membrane process. The results obtained during this work indicate that UF is a viable separation process for the treatment of bilge water for compliance with overboard discharge regulations.

INTRODUCTION

The treatment and recycling of waste materials are essential in order to reach the goals of sustainable development. Synthetic membranes are well suited to perform these tasks. Membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) do not involve phase changes and as a result have low overall energy utilization. Separations can occur at or below room temperature, which reduces the degradation of temperature sensitive compounds. The presence of a physical barrier between the waste and product stream assures product quality and the design of membrane systems is modular which facilitates scale-up.

The release of oily wastewaters originating from a ship's bilges is of particular environmental importance as evidenced by the more stringent regulations for the release of bilge water to the environment. Seawater and freshwater are constantly entering a ship's bilges and must eventually be discharged. In the absence of effective onboard treatment facilities this necessitates discharge to shore based treatment facilities or barges which may or may not have treatment capabilities thus adding significantly to the cost of discharge. Bilge water is a complex and highly variable mixture of several components such as seawater, lubricating oil, greases, marine diesel fuel, hydraulic oil, detergents, metal oxides (rust particles), corrosion inhibitors, asbestos and other insulation particles, refrigerants and other wastes.

Bilge water is usually treated by settling followed with coalescence. It is first gravity separated in a parallel plate separator and coalesced in a series of hydrophobic filters to promote the agglomeration of oil droplets. In practice the ship's movement affects the efficacy of the plate separators. In several instances this method of treatment produces an effluent that does not meet the requirements for overboard discharge.

Ultrafiltration has been used for over two decades in the treatment and recycling of spent cutting oils. Cutting oils are a mixture of lubricating oils and surfactants. The use of membranes in this application is well established and commercially available.

Treating cutting oils with ultrafiltration is relatively simple as the quality of the oil/water emulsion is high and can be controlled by proper formulation. The particulates present in the cutting oil are relatively large and are easily filtered out before they reach the membrane. In an application treating bilge water, the content of the waste, its composition or strength cannot be controlled. The quality of the oil/water emulsion is poor since bilge water containing oil, phase separates quite readily.

The use of ultrafiltration to treat bilge water is relatively new. The objective of this work is to study the performance of UF membranes when separating oily wastewater of similar composition and strength to that of bilge water found aboard HMC ship's.

DEFINING BILGE WATER

In practice, there exists considerable ship to ship and time variations in the composition and strength of bilge water. Performing membrane permeation tests on a sample of bilge water from one ship does not necessarily provide treatability estimates for all ships in the Canadian Navy. The use of synthetic mixtures, provides an insight into the effect of various components on membrane performance.

A study conducted on behalf of the Canadian Navy determined the average composition of bilge water to be (Resera. 1995):

a) total oil and grease TOG= 1,284 mg/L;

b) Total suspended solids (solids > 0.45 microns) TSS = 502 mg/L;

c) Total dissolved solids (solids < 0.45 microns) TDS = 17,730 mg/L

Waste audits were previously performed by the Canadian Navy to identify the materials that are most likely to be found in bilge water. This lead to the definition of a synthetic bilge water cocktail defined as follows:

a) oils – 2000 ppm. Composed of the following Canadian Navy standard oils: 50% naval distillate (diesel fuel), 40% naval diesel engine lubricating oil and 10% hydraulic oil;

b) detergents and surfactants - 500 ppm. Composed of 90% Canadian Navy standard oil and grease detergent (CLEANBREAK) and 10% Canadian Navy standard corrosion removal compound (OSTREM Rust Stain Remover); and

c) water - remaining 99.7%. Composed of a 50/50 mixture of fresh and sea water.

Lubricating oil found in bilge water originates from the crankcase of diesel engines aboard ships. In a preliminary test, the ability of UF membranes to separate a bilge water mixture containing either new or used oil was studied. The bilge water mixture was mixed and treated in a stir cell with a membrane having a molecular weight cutoff (MWCO) of 20,000 Daltons. The permeate flux for the new and used oil vs. time are plotted in Figure 2.1.

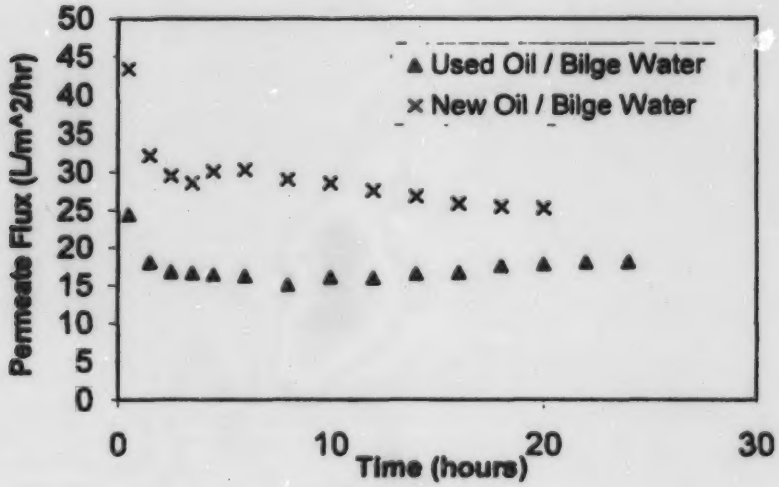

Figure 2.1 – Plot of permeate flux vs time for a 20,000 Dalton MWCO membrane.

As seen in Figure 2.1, a very steep initial decline in permeate flux occurs for the test using used oil. Membrane flux using used oil remained nearly half of that of new oil over the first 15 hours of the test and remained lower over the next 9 hours of the membrane test. As used oil is found in bilge water, it was used in all further tests.

Particulates in used oil

Used lubricating oils originating from internal combustion engines contain particles of soot formed during the combustion process. The initial size of these soot particles depends on the conditions existing in the combustion chamber at the time they were formed. Their size is difficult to estimate but carbon black particles are commercially available with average particle sizes ranging from 8 to 100 nm and a specific gravity of 1.7 to 1.9 (Columbian Chem. Co., 1997). Once formed, the carbon black particles can aggregate into larger units measuring several microns. The oil filter in a diesel engine will limit the size of soot particles present in used oil. Most oil filters in diesel engines have a nominal rating of 5 to 8 microns with an absolute cutoff of 24 microns.

Under normal operation, the larger openings in an engine's oil filter will have greater amounts of oil flowing through them than the smaller openings. Soot particles will tend to bridge in these channels and decrease the size of the openings, improving the filter's rating. This is verified by the observation of used oil under an optical microscope where the largest particle observed measured five microns. Soot particles were observed from 5 microns down to sizes well beyond the resolution of the optical microscope as evidenced by a uniform gray background in the entire field of view of the microscope.

THEORY

Membrane performance is governed by a variety of factors. Some of these are ability to separate solutes, intrinsic resistance to flux, system operating conditions such as transmembrane pressure and cross-flow velocity and solution/mixture characteristics such as viscosity and solute fraction. An understanding of the relative contributions and mechanisms of the various resistive components can provide insight into what aspect of system resistance should be targeted in order to increase membrane system efficiency.

For liquid separation, permeate flux (J) is known to be a function of operating (transmembrane) pressure (ΔP), fluid viscosity (μ) and the system's overall resistance (R_{total}) to permeation. Membrane flux can be expressed in terms of resistances as follows (Mulder, 1995):

$$J = \frac{\Delta P}{\mu R_{total}} \tag{1}$$

The total system resistance is the cumulative effect of the system's various resistive components. These resistive components are:

a. membrane resistance - R_{mem};

b. filter cake (or gel or membrane boundary) layer resistance - R_{cake};

c. resistance due to membrane fouling - R_{foul}.

The total system resistance can be expressed as (Mulder, 1995):

$$R_{total} = R_{mem} + R_{cake} + R_{foul} \tag{2}$$

Membrane Resistance

In ultrafiltration (UF) and microfiltration (MF) applications, the permeate flux for a new membrane, in the absence of any solutes or particulates, is solely limited by membrane resistance. This is commonly referred to as a membrane's "pure water permeate" flux (J_{PWP}). Permeation of pure water through a clean membrane, is expressed as (Eykamp, 1995):

$$J_{PWP} = \frac{\Delta P}{\mu R_{mem}} \tag{3}$$

Concentration Polarization

During membrane separations, concentration polarization occurs at the surface of the membrane. Concentration polarization is the build up of solute at the surface of the membrane causing a gradient in concentration at its surface. When particles are present, this results in the build up of a cake, or gel, layer at the surface of the membrane. As the filtration run proceeds, this cake layer continues to grow, resulting in a reduction in permeate flux. The thickness of the cake layer reaches a steady state value when the flow of solute or particles towards the cake layer equals the diffusion of solute or particles away from the cake layer. A boundary layer is present above the cake layer where the solute concentration is in transition from the bulk to the greater cake layer concentration.

The degree of concentration polarization will be affected by the mass transfer conditions existing in the flow channel above the membrane, the flux through the membrane and membrane pore size; with limiting cases being for large and small pores. For membranes with relatively large pores the flux will be high and therefore the effect of concentration polarization will be important. For membranes with relatively small pores membrane flux will be low and therefore the degree of concentration polarization will also be low (Mulder, 1995).

However, the mass transfer co-efficient is strongly influenced by the operational (hydrodynamic) characteristics of the system. Specifically, the mass transfer co-efficient is defined as the ratio of the diffusion co-efficient (D) and the cake layer thickness (δ) and can be expressed as :

$$K = \frac{D}{\delta} \tag{4}$$

Cake Layer Resistance

As described above, the cake layer is the result of concentration polarization phenomena. It is a thin film, lying directly on the membrane surface. This cake layer provides additional filtration properties and its resistance can be described as (Davis, 1992):

$$R_{cake} = \hat{R}_{cake}\delta \tag{5}$$

Where $\hat{R}_{cake}$ is the specific cake layer resistance and δ is the cake layer thickness.

Several means of evaluating the specific cake layer resistance exist, one of which is estimation by means of the Blake-Kozeny equation (Davis, 1992):

$$\hat{R}_{cake} = \frac{37.5\phi_{max}^2}{a_p^2(1-\phi_{max})^3} \tag{6}$$

Where ϕ_{max} is the maximum solute volume fraction of the cake layer and a_p is the radius of the solute particle. The cake layer thickness can be determined from the maximum solution volume fraction and the solute particle size. For rigid spheres, the maximum solute volume fraction is known to be 0.58 (Sethi and Wiesner, 1995) therefore the only remaining variable needed to determine the specific cake layer resistance is the solute particle radius.

If a solution, such as bilge water, is composed of a range of different particle sizes, the particle most likely to be found in the cake layer will be the one having the lowest diffusivity. The total diffusivity of a particle in solution is the sum of its Brownian (D_{bm}) and Shear (D_{shear}) diffusivities, defined as (Davis, 1992, Sethi and Wiesner, 1995):

$$D_{bm} = \frac{kT}{6\pi\mu a_p} \tag{7}$$

$$D_{shear} = \dot{\gamma}\, a_p^2\, (0.33\phi^2(1+0.5e^{8.8\phi})) \tag{8}$$

Where k is Boltzmann's constant, T is temperature and $\dot{\gamma}$ is the local shear rate. The local shear rate is the velocity gradient within the cake layer and can be expressed as (Davis, 1992):

$$\dot{\gamma} = \frac{\tau_w}{\mu\eta(\phi)} \tag{9}$$

Where τ_w is the wall shear stress and $\eta(\phi)$ is the relative viscosity.

For flow in a lumen of circular cross section the wall shear stress and the relative viscosity are defined as (Sethi and Wiesner, 1995):

$$\tau_w = \frac{4U\mu\eta(\phi_b)}{r_i - \delta} = \frac{\tau_{wo} r_i^3}{(r_i - \delta)^3} \tag{10}$$

$$\eta(\phi) = \left(1 + \frac{1.5\phi}{1 - \frac{\phi}{0.58}}\right)^2 \tag{11}$$

Where U is the cross-flow velocity and r_i is the radius of the membrane flow channel.

A system's variables that can alter the cake layer's diffusivity are the cross-flow velocity and solute concentration (i.e. the concentration of oil in bilge water). Figure 2.2 is a plot of the total diffusivity of a particle versus particle size, for a solute volume fraction within the cake layer of 0.29, a cross-flow velocity of 0.9 m/s and a particulate concentration of 250 mg/L.

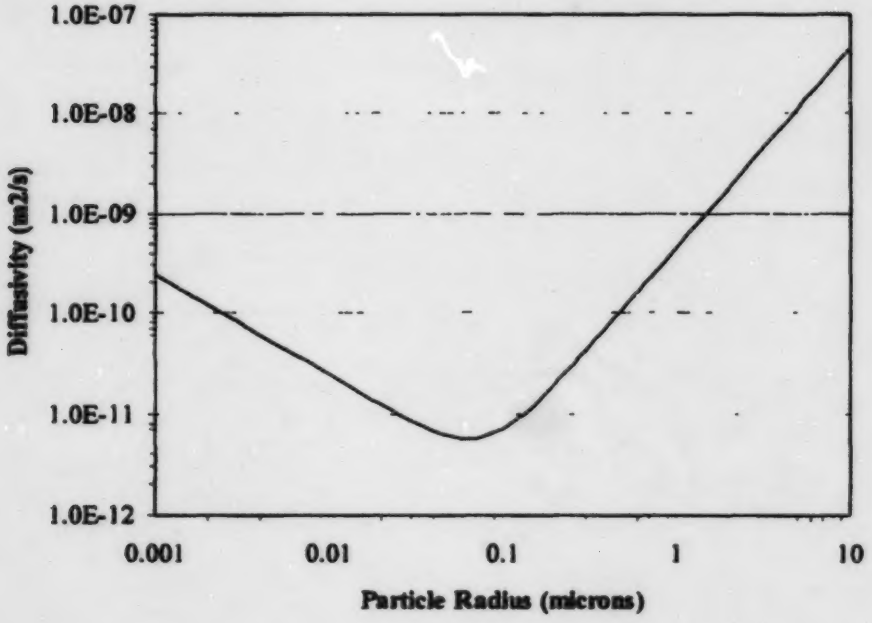

Figure 2.2. Effect of Particle Size on Cake Layer Diffusivity

As seen in Figure 2.2 the critical particle radius, associated with a minimum diffusivity, is below 0.1 micron – approximately 0.065 micron. While it is impossible to identify a precise critical solute particle size it is reasonable to expect that the range of critical solute particle sizes, for MF and UF will be approximately 0.01 to 0.1 microns.

EXPERIMENTAL METHOD

Various commercial flat sheet membranes were tested in a 7 cm diameter stir cell operated at 345 kPa (50 psig) and 25.0 °C and controlled to +/- 0.1 °C. Permeate flux was determined with an autosampler. The membranes were obtained from Koch Membranes (Ann Arbor, Michigan, USA) and OSMONICS (Minnetonka, Minnesota, USA). In most cases some details, such as the material forming the selective layer, was not available. The "G" series membranes produced by Osmonics were of the thin film composite type. The M100 and P707 membranes produced by Koch Membranes were made from polyvinylidine difluoride (PVDF).

Additionally, membrane selectivity was not always expressed in the same manner by the manufacturers, that is, most of the membranes had their selectivity expressed in terms of MWCO(molecular weight cut-off), others were given in terms of pore radius in nanometers. The correlation between MWCO and pore radius is dependent upon the polymer used to determine the MWCO. For polyethylene glycol (PEG) and polyethylene oxide (PEO) the correlation between MWCO and solute size (Tremblay, 1992) was used to determine pore radius.

RESULTS AND DISCUSSION

The key objective of this work was to examine the effect of nominal membrane pore sizes on membrane flux when treating the synthetic bilge water mixture. Flat sheet testing also provided insight as to whether flux was dominated by membrane or cake layer resistive components. Membrane flux data after one hour of operation were compared. Assuming minimal fouling during the initial operation of the system, the cake layer resistance can be determined using these flux values. Results obtained earlier in the run are closer to those of dead-ended filtration and are more accurately modeled by the equations derived in the previous section. The initial membrane's intrinsic resistance was identified from pure water permeate runs. These results were included in Table 2.1.

Table 2.1. Membrane pore radius, pure water permeate flux and flux after 1 hour, and the resistive components of the membrane and cake layer.

Membrane			PWP Flux	Flux at 1hour and 345 KPa	Membrane Resistance	Cake Layer Resistance
Name	MWCO (Daltons)	pore radius (nm)	at 345 KPa ($L/m^2/h$)	($L/m^2/h$)	(10^{14} m^{-1})	(10^{14} m^{-1})
GH	2,500	2.0	6.15	4.0	2.32	0.61
GK	3,500	2.2	33.1	5.23	0.42	2.24
GM	8,000	3.3	54.2	3.57	0.26	3.64
GN	10,000	3.7	105	17.4	0.13	0.67
M100	20,000	5.2	217	24.6	0.084	0.48
QW	30,000	6.4	207	19.2	0.070	0.66
P707	150,000	14	329	37.4	0.042	0.33
QX	3,600,000	70	439	34.2	0.023	0.38

Solute Particle Size

The cake layer resistance, in simple terms, is defined as the product of the specific cake layer resistance and cake layer thickness, as defined by equation 5. Therefore, differences in the cake layer resistances, identified above in Table 2.1, are due to changes in the specific cake layer resistance, the cake layer thickness or both of these variables. For each of the membranes, the specific cake layer resistance is a relatively constant value, as it is defined by the solute particulate size and the solute volume fraction of the cake layer (equation 6). Whereas the cake layer thickness varies with membrane pore size.

If the solute size and volume fraction in the cake layer remain constant then the specific cake layer resistance is expected to remain constant. Therefore, for each individual membrane, changes in cake layer resistance should be dictated by changes in the cake layer thickness.

Provided a membrane can retain the solute particles it is intended to separate from the solvent, i.e. for bilge water, it is desired to separate oil emulsions and other particulates from water, the cake layer thickness, and therefore its associated resistance should increase as MWCO increases. This is because as pore size increases the flux of water through the membrane increases. This increase in flux results in a greater degree of concentration polarization at the membrane's surface and therefore a thicker cake layer. However, if the pore size is large enough to allow particulates or oil emulsions to pass through it, the cake layer thickness will decrease with increasing membrane pore size as the membrane no longer retains the particulates or oil emulsions.

Examination of the cake layer resistive values in Table 2.1 does not reveal a continually decreasing cake layer resistance, but two distinct membrane groupings. For membranes with a MWCO less than 8,000 Daltons, the cake layer resistance increases with increasing MWCO. However, for the membranes with a MWCO greater than 8,000 Daltons the cake layer resistance does not continue to increase. For membranes with a

MWCO larger than 10,000 Daltons a significant drop in the cake layer resistance is noted; as compared to the cake layer resistance for membranes with a MWCO less than 8,000 Daltons.

It is expected that an oil emulsion will be no smaller than 0.035 microns(35nm) in diameter (Lipp et al, 1988). As seen in Table 2.1 only the QX membrane has a nominal pore size greater than this size, therefore if only oil emulsions were present in the bilge water one would expect to observe an ever increasing cake layer resistance, but this does not occur. This suggests that the unexpected cake resistance trend is due to the presence of different particles in the synthetic bilge water mixture.

As previously discussed, the cake layer thickness, and therefore the cake layer resistance, can be estimated using equations 5 and 6. Many of the variables contained in equation 5 are known or can be readily determined. However, the maximum solute volume fraction in the cake layer, the steady state time and the particle size are unknown.

The maximum solute volume fraction in the cake layer is assumed as a constant value of approximately 0.58 – true for non-deformable spheres (Sethi and Wiesner, 1995). The permeate flux of the membranes were compared after one hour of operation. The remaining known variables in equation 5 can be used to solve for the particle size. The unusual behaviour of the cake resistance vs molecular weight plot suggests that two populations of particles or emulsions were present in the bilge water. The sudden drop in cake resistance from 8,000 to 10,000 Daltons MWCO suggests that a population of smaller particles exist whose size is in between the pore diameter of these membranes. The radius of the smaller particles was taken as 3.5 nm, the average radii of the GM and GN membranes.

The size of the larger particles was determined by performing a least squares fit of equations 5 and 6 to the cake resistance for membranes having a MWCO >= 10,000 Daltons. The results gave a particle radius of 25 nm which is in close agreement with Lipp et al, 1998. The model provided an excellent fit to the data as shown in Figure 2.3.

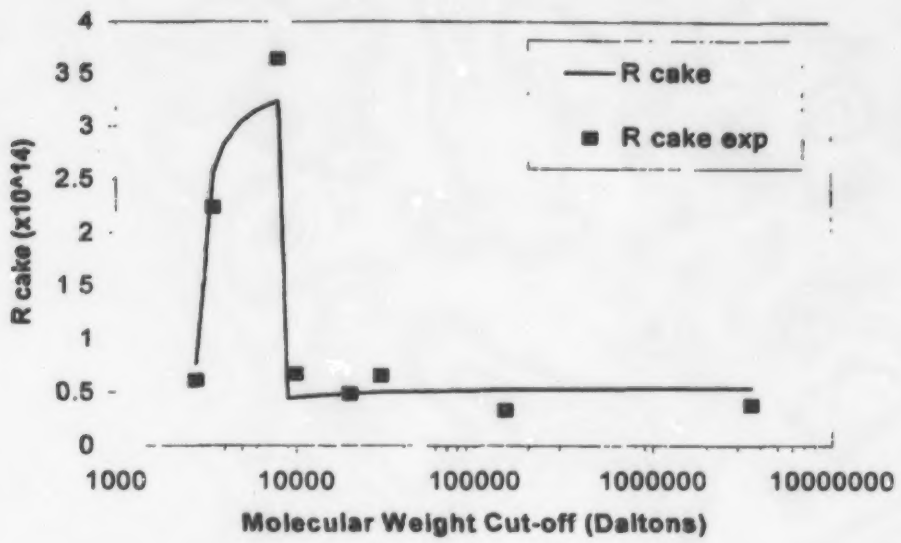

Figure 2.3: Cake layer Resistance experimental and fitted vs. Membrane MWCO.

The particulate radii of 3.5 nm and 25 nm, are important in that they provide clues as to the nature of these particles. As identified, from a literature review it is not expected that an oil emulsion will have radius less than 17.5 nm (Lipp et al, 1988). Therefore it is not likely that the smaller solute particle, radius of 3.5 nm, is an oil emulsion. Some likely sources of these smaller particles is soot which can be as small as 4 nm in radius (Columbian Chem. Co., 1997). The larger solute particles are likely to be oil emulsions but could also be soot.

However. the particles of an oil emulsion cannot be expected to retain a constant size. The mixing, associated with pumping, and the presence of surfactants in the bilge water will counteract the agglomeration of oil emulsions and therefore bilge water will be

comprised of a size range of oil emulsions. As shown by Lipp et al. the size of an oil emulsion can reasonably be expected to have a size ranging from 35 and 450 nm, with the emulsion size depending on a number of variables, including oil and surfactant content (Lipp et al, 1988). However, the size of oil emulsion within the cake layer should not have as great a range as the size in the bulk bilge water solution. As previously illustrated in Figure 2.2, the particle having the lowest diffusivity will be preferentially retained at the surface of the membrane.

Both soot and oil were found on the surface of the membranes with MWCO's above 2,500 Daltons. Photomicrographs of the surface of the GN membrane, after 24 hours of operation, reveal the presence of oil and a large number of particulates. On visual observation, the membranes were covered by a mixture of greasy soot particles. Further work is required to determine which component is most seriously contributing to the gel limiting flux observed for membranes having MWCOs above 10,000 Dalton.

These results indicate that a membrane having a molecular weight cut-off above 10.000 Daltons should be used in this application. The 3.5 nm particles of soot should not be retained by a membrane used in an oily water separator, as soot is present in all diesel exhaust and is not regulated in this context. Although the 3.5 nm soot particles may act as nucleation sites for oil droplets they do not add an appreciable amount of oil to the permeate as all membranes tested met the oil contamination level regulations.

CONCLUSIONS

Particles of soot present in bilge water impose serious constraints on the treatment of this wastewater using UF membranes.

The following conclusions can be drawn from this work;

1. The permeation of water through UF membranes was found to be entirely cake/gel limited.
2. Based on the permeate flux after 1 hour of operation, two populations of particles having 3.5 and 25 nm radii were found to affect the permeate flux of UF membranes.
3. The smaller particles are likely to originate from soot while the larger particles could be soot, oil emulsions or a mixture of both.
4. A membrane having a MWCO above 10,000 Daltons should be used in this application to allow for the passage of the 3.5 nm particles which cause very high cake resistances.

ACKNOWLEGMENTS

The authors wish to thank the Defence Research Establishment Atlantic (DREA) for supporting this work.

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SECTION 3 SEM and XPS examination of the cake layer.

SEM Examination of the cake layer

The surface of membranes after treating the half hour and 24 hour settled bilge water in the 0.07 m diameter stir cell were examined by Scanning Electron Microscopy. The higher resolution micrographs show a large number of fine particles in the <0.2 micron size. This can be seen in Figures 3.1 to 3.4 for the GK, GM, GN and GH membranes. Many small particles measuring less than 0.2 microns in diameter are present in the filter cake. This is in good agreement with the DLS measurement of 89 nm radius and the filter cake calculations in Table 1.2.

The micrographs taken at lower resolutions indicate a cake layer that has de-phased on drying leaving a very open structure. The micrographs in Figures 3.5 to 3.11 show that the cake retained some structure on drying. Free oil would be expected to smear and leave an entirely smooth, oily, surface. These cakes contain a considerable amount of hydrophylic substances that maintain water into their structure on drying. The presence of particulates in the cake could also contribute to the resulting porous structure of the cake. The composite nature of the cake is further seen by looking at the x2000 and x5000 magnifications as seen in Figures 3.12 to 3.24. The presence of only particulates in the cake layer would have produced a structure with imbedded particles as in Figure 3.20 which was taken inside a hole through the surface of the cake. These results indicate that the cake is formed from both chemically emulsified oil and particulates of soot.

As seen in Figure 3.5, the oily cake is not present on the GH membrane, residual salts remaining on the surface of the membrane crystallized on drying. These larger crystals were not observed on other membranes indicating that the salts remained well dispersed in the cake layer on drying. This suggests that the filter cakes could contain reverse miscelles resembling the structure of a grease. The presence of reverse miscelles in a cake leads to more closed cake structures. The quality of the emulsion present in bilge water will affect the optimal, long term, operation of the process.

a)

b)

Figure 3.1 Surface of a GK membrane after a 24 hour filtration run. Bilge water settled for a) ½ hour and b) 24 hours.

Figure 3.2 Surface of a GM membrane after a 24 hour filtration run.
(24 hour settling).

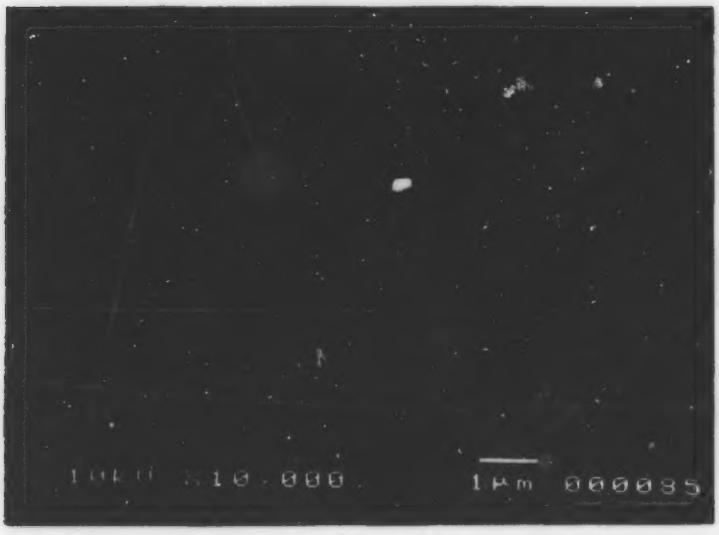

Figure 3.3 SEM of the surface of a GN membrane after a 24 hour filtration run.
(24 hour settling).

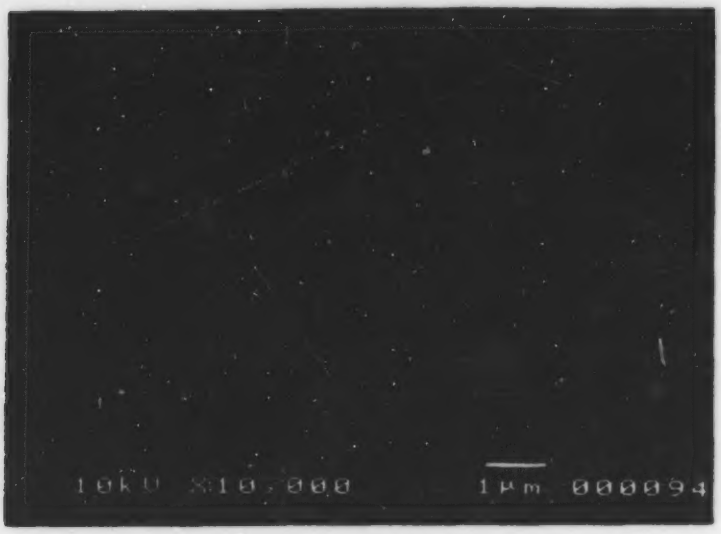

Figure 3.4 SEM of the surface of a GH membrane after a 24 hour filtration run. (24 hour settling).

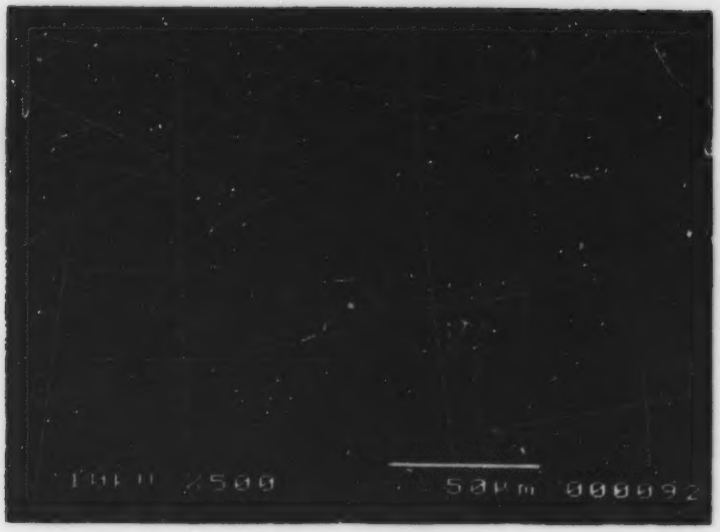

Figure 3.5 SEM of the GH membrane showing salt crystals but no oily film. (24 hour settling).

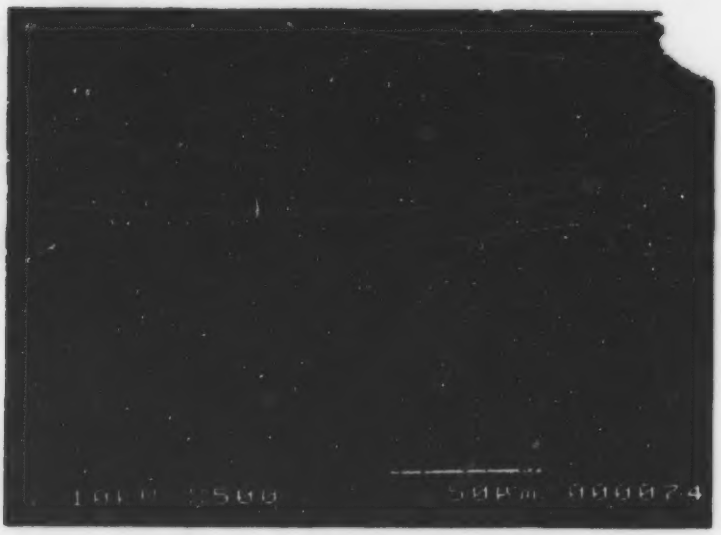

Figure 3.6 SEM of the GK membrane (24 hour settling).

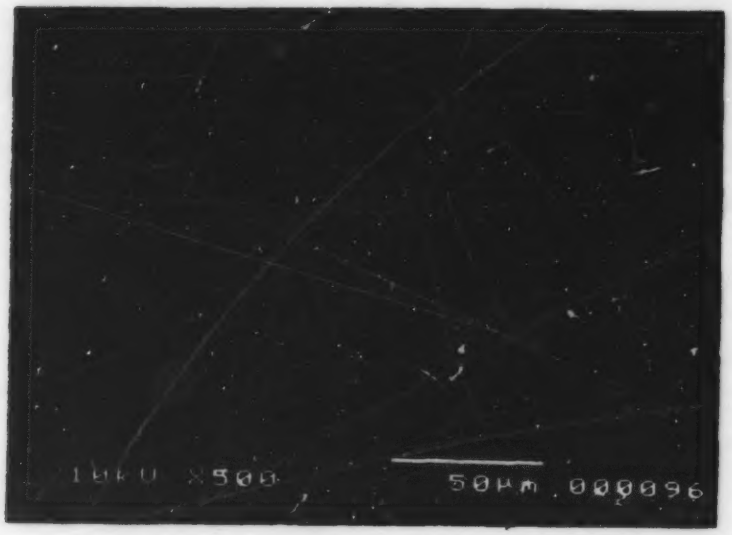

Figure 3.7 SEM of the GN membrane (24 hour settling).

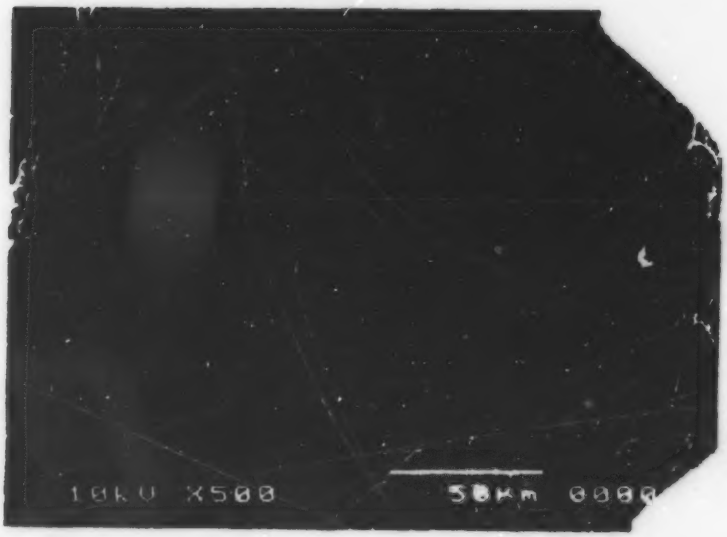

Figure 3.8 SEM of the QW cake on the QW membrane (24 hour settling).

Figure 3.9 SEM of the cake on the surface of a GK membrane (½ hour settling).

Figure 3.10 SEM of the cake on the surface of a GM membrane (½ hour settling).

Figure 3.11 SEM of the cake on a GN membrane (½ hour settling).

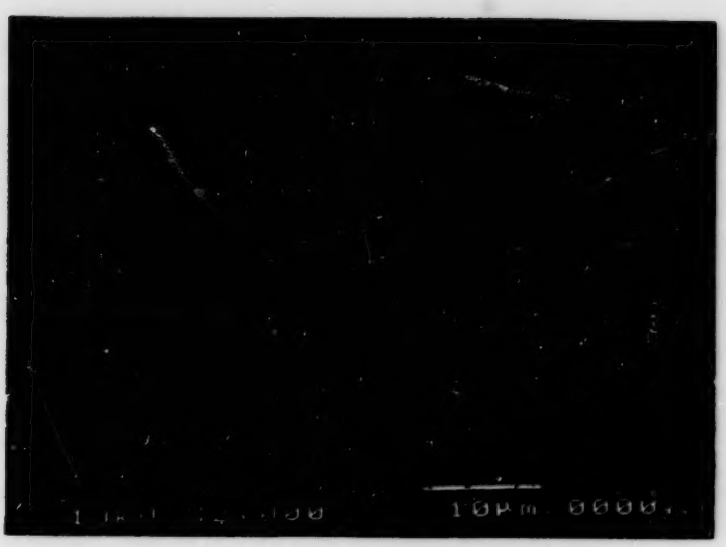

Figure 3.12 SEM of the cake on the surface of a GK membrane (24 hour settling).

Figure 3.13 SEM of the cake on the surface of a GN membrane (24 hour settling).

Figure 3.14 SEM of the cake on the surface of a QW membrane (24 hour settling).

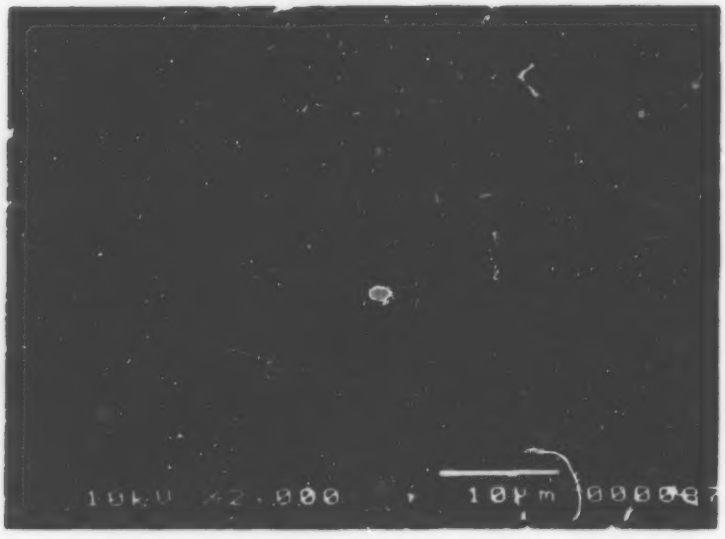

Figure 3.15 SEM of the cake on the surface of a GK membrane (½ hour settling).

Figure 3.16 SEM of the cake on the surface of a GM membrane (½ hour settling).

Figure 3.17 SEM of the cake on the surface of a GN membrane (½ hour settling).

Figure 3.18 SEM of the surface of the GH membrane (24 hour settling).

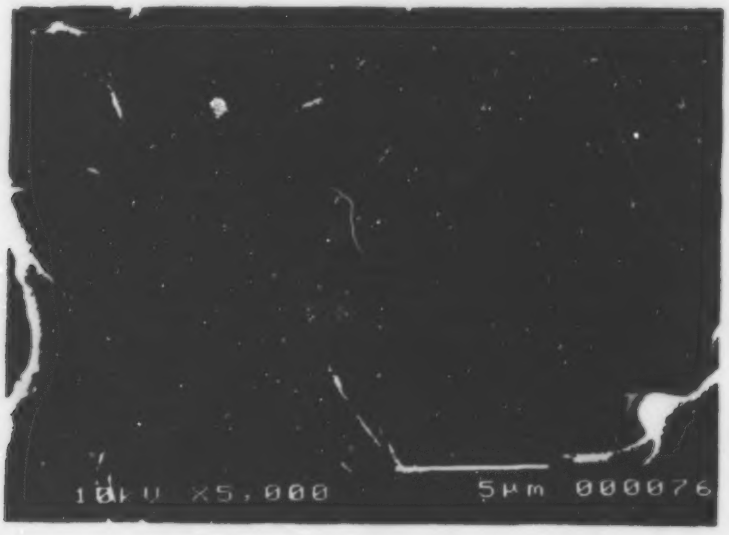

Figure 3.19 SEM of the surface of the GK membrane (24 hour settling).

P515557.PDF [Page: 87 of 154]

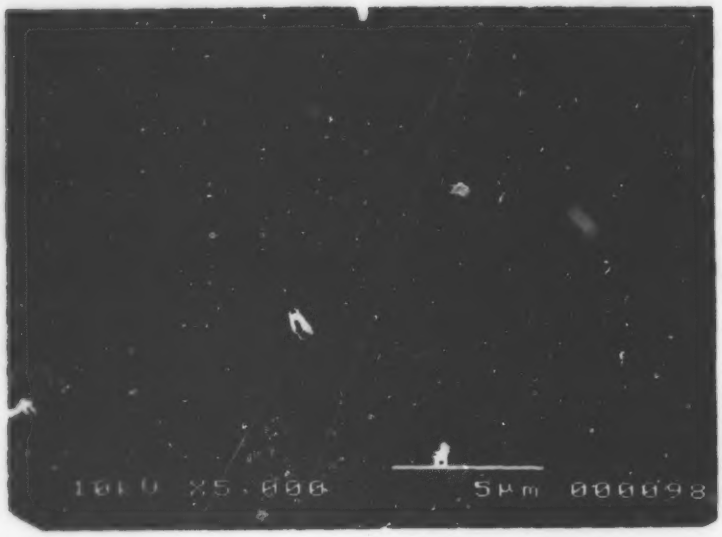

Figure 3.20 SEM of the surface of the GN membrane (24 hour settling).

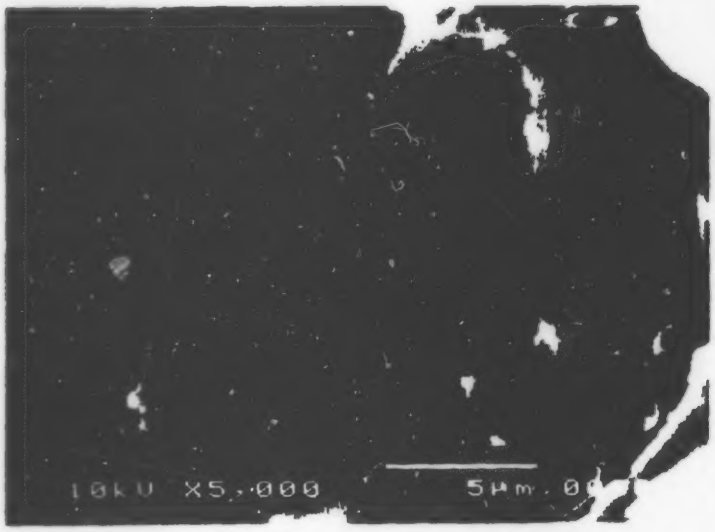

Figure 3.21 SEM of the surface of the QW membrane (24 hour settling).

Figure 3.22 SEM of the surface of the GK membrane (½ hour settling).

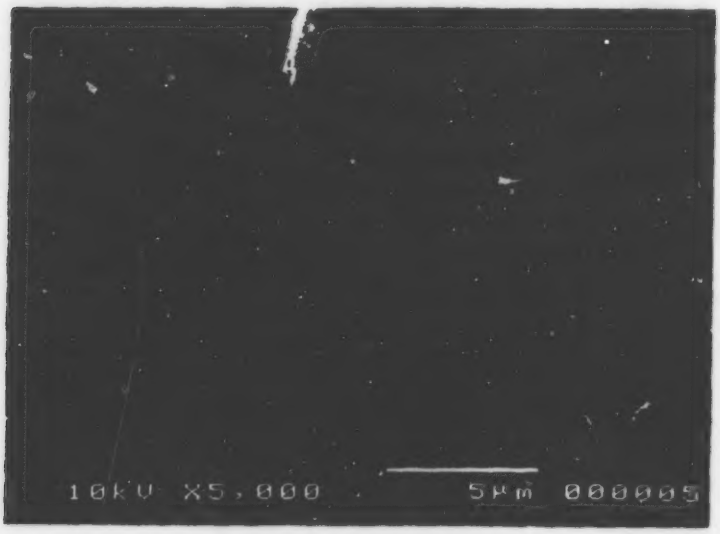

Figure 3.23 SEM of the surface of the GM membrane (½ hour settling).

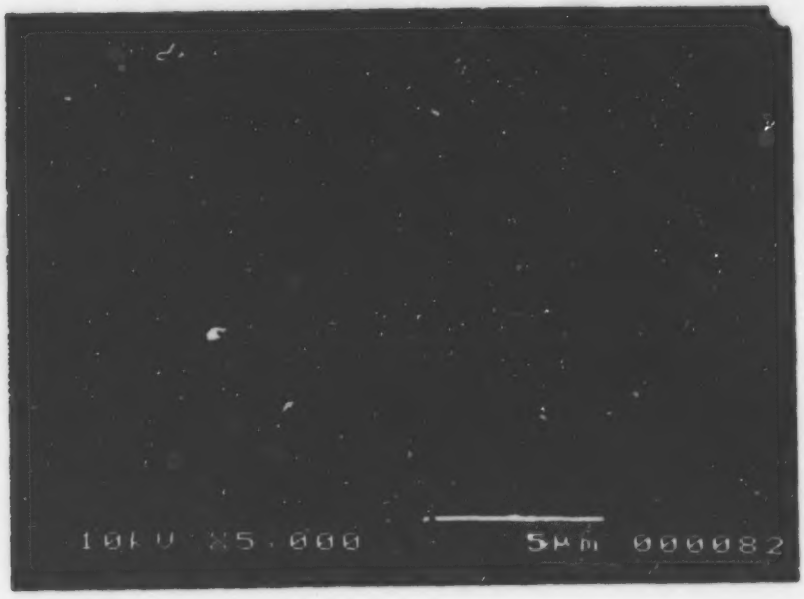

Figure 3.24 SEM of the surface of the GN membrane (½ hour settling).

XPS measurements of the filter cakes

XPS measurements were performed on the surface of the GK and GN membranes. A small piece of membrane with a "clean" edge and membrane covered by the filter cake was mounted on an analysis tube with a clip and pumped for about 20 min to 10^{-8} Torr, then admitted into the analysis chamber. Analysis was less than 10^{-8} Torr in the chamber of the Kratos Axis XPS using monochromated AL K α x-radiation. Charge neutralization was used since the samples are non conducting.

A survey was run to identify elements present then each element was run at high resolution for peak shape, position and quantification. For both membranes, two areas were measured and the results averaged and reported in atomic % keeping in mind that XPS does not detect hydrogen and is not included in the 100 atomic %. Table 3.1 below lists the results of this analysis.

Table 3.1. Results of the XPS analysis.

Sample	GK clean	GK dirty	GN clean	GN dirty
Total carbon	71.6	79.6	79.5	79.7
C 1s at 285.0 eV	48.2	61.7	60.8	67.4
286.5	14.2	11.9	13.2	8.4
287.5	5.3	3.2	3.4	2.9
288.7	3.9	1.9	2.2	
Oxygen	21.2	17.1	16.5	15.0
Sodium		0.6	0.2	0.6
Chlorine	2.3	0.6	0.5	0.3
Silicon	1.1	1.6	0.9	1.7
Nitrogen	2.5	0.8	1.8	1.2
Sulfur	1.0	0.8	0.7	1.5
Magnesium	0.4			

Metals such as iron, vanadium, molybdenum or manganese were not detected on either the GK or GH membranes. Either the concentrations of these metals are too low for XPS detection or they are covered by 75 Å of material. As previously seen in the SEM micrographs the filter cakes offered an open structure on drying so that the underlying surface of the cake would have also been detected in the XPS test. Carbon was the major element present on the "clean" surface and on the cake. The high resolution measurement of the C 1s peak does show some difference between the clean and dirty samples. Peak positions were corrected to 285.0 eV for saturated carbon. In the GK there was a substantial increase in this peak which suggests that a relatively clean portion of the membrane was seen. The increase indicates that a layer of saturated hydrocarbon is present on the filter cake. In the GN membrane the trend was the same but not as pronounced as the GK membrane.

Other elements such as sulfur could come from the sulfates present in the bilge water while nitrogen which is higher in the "clean" membrane than on the cake can be attributed to the Thin Film Composite membrane usually produced from polyamide. The oxygen could originate from the detergents and possibly from the hydrolyzed used oil.

SECTION 4 Silt Density Measurements.

In order to estimate the degree of difficulty in separating bilge water, a mixture containing the 2000 mg/L of oil and 500 mg/L detergents was prepared, circulated using a centrifugal pump for one half hour and allowed to settle for one half hour. The mixture was then passed through a 0.45 micron filter and the flow recorded as a function of time. In a normal Silt Density Index (SDI) measurements, the time required to filter 500 mL of feed and the time required to measure an additional 500 mL of feed are used to calculate this value. In the case of bilge water, the filter plugged up after 125 mL of permeate passed through and little if any permeate flowed through the filter after that. It was deemed useless to obtain a SDI value for the bilge water, as it contains too many particles. The prescribed method to follow here would be pretreatment to reduce particulate matter before such a feed is sent to a RO, NF or UF system.

SECTION 5

The ability of membranes to separate oil and grease

The membranes listed in Table 1.1 were placed in a cross flow cell operated at a cross-flow velocity of from 1 to 1.8 m/s. Permeate was analyzed and the results are listed in Table 5.1 below. The results indicate that all membranes produce a permeate that meets and greatly exceeds the discharge regulation of 15 mg/L oil and grease for a feed concentration of 73 mg/L oil and grease.

Table 5.1 – Membrane MWCO, and Hexane extractable oil and grease in the permeate. Membranes were tested at 50 psig. Bilge water concentration of hexane extractable Oil and Grease EPA 1664 = 73 mg/L

Membrane		Volume tested (L)	Hexane extractable oil and grease (mg/L)	% Separation based on Hexane extractable oil and grease (mg/L)
Name	MWCO (k Daltons)			
GH	2.5	155*	6.5	91.2
GK	3.5	423*	0.9	98.7
GM	8.0	1000	1.4	98.1
GN	10.0	680	0.9	98.8
M100	20.0	1074	0.1	99.9
QW	30.0	1011	0.2	99.7
P707	150.0	1026	0.1	99.9
QX	3,600.0	998	0.2	99.7

*Both coupons had very little flow at 50 psig these volumes were produced over a 48 hour period.

The quality of the permeate was independent of the molecular weight cut-off of the membrane. This clearly indicates cake dominated filtration. Although the amount of permeate tested for the GH membrane is very low, the relatively large amount of oil passing through the membrane coincides quite well with the observations deduced from Figures 3.5 to 3.8 where a cake was not observed for the GH membrane and a cake was observed for all other membranes. The pore radius of the GH membrane is 2.0 nm which should have separated 40 nm particles. This suggests that some oil is dispersed at the molecular level or is destabilized on contact with the membrane but is scrubbed clean from solution as the feed passes through the cake. In essence, the cake enhances the separation of free oil by capturing it in its structure. This suggests that the state of the emulsified oil be it chemical or mechanical forming the cake will affect the separation process. The 24 hour settled bilge water offers a cake having a more closed porous network, Figures 3.19 to 3.21, than the cake obtained from the half hour settling, Figures 3.22 to 3.24. The cake layer acted as a dynamic membrane. This type of membrane can be formed dynamically and regenerated. Further studies are required to verify the role of the cake as a dynamic membrane in removing the <2.0 nm radius oil and grease particles from the feed stream.

SECTION 6

Tests to determine the influence of oil-membrane surface interactions

In order to verify that free oil was not irreversibly coating the surface of the membrane, experiments were performed where free oil was poured directly onto the surface of the membrane prior to the permeation run. This experiment was conducted in the same 7.0 cm diameter stir cell. The QW membrane was selected for these tests. In this experiment, the membrane was initially wet with water. Water droplets were completely removed from its surface. The membrane was placed in the stir cell and oil was poured directly onto the membrane until it was coated by a 1/8" thick layer. The oil covered membrane was then allowed to sit for 5 minutes. The stir cell was filled with bilge water and a standard permeation experiment carried out at 50 psig.

As seen in the Figure 6.1 below, initially the flux was lower than that of the untreated membrane. For new oil, flux recovered within one hour and followed the same decay pattern as that of the untreated membrane. For used oil, the flux recovered after 5 hours but eventually declined to the same flux as that of the untreated and new oil tests.

This indicates that new oil does not readily adsorb and block membrane pores. This clearly demonstrates that new oil is not limiting permeability at this MWCO (which is close to the 50,000 Daltons presently used aboard HMC ships).

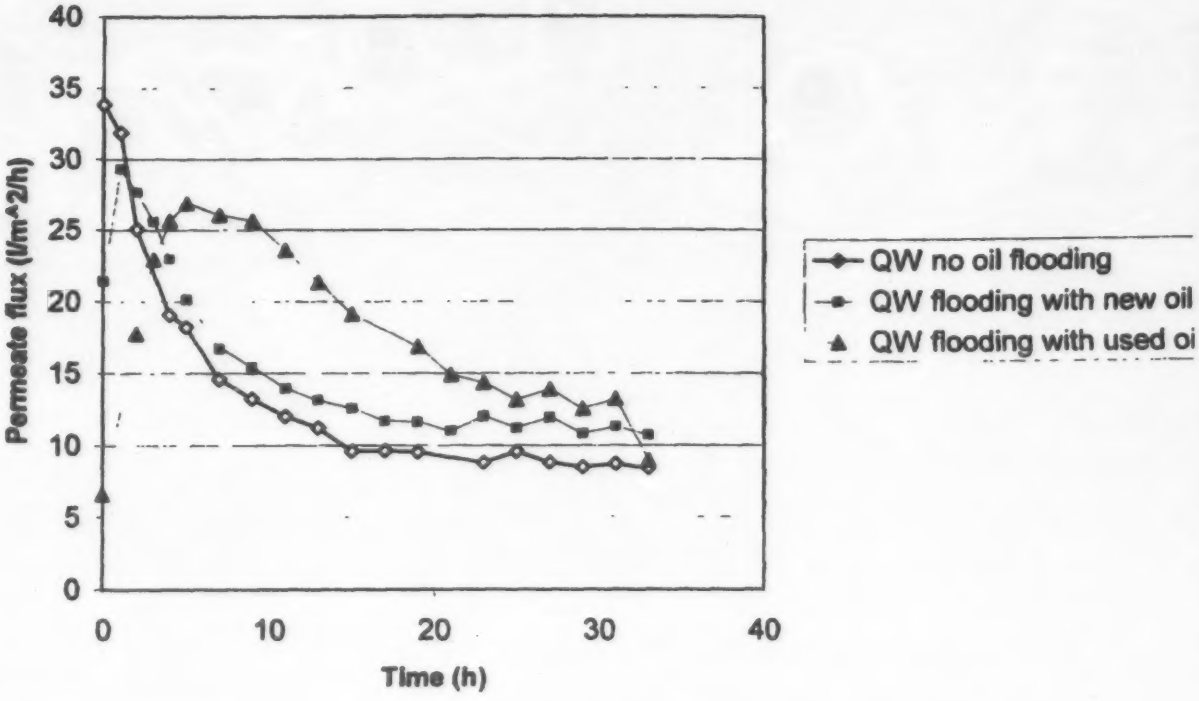

Figure 2.1. Plot of permeate flux vs. time for a membrane flooded with oil.

To determine the affinity of oil for the membrane, the test described above was repeated with used oil in the absence of pressure. After a period of 24 hours in the stir cell, 90 % of the membrane surface was free of oil and just as clean as at the beginning of the test.

These tests indicate that the membrane can recover from the de-phasing of free oil at its surface. Also that hydrophilic membrane materials do exist, such as that used in the fabrication of the QW membrane, that reduce or eliminate free oil as a cause of membrane fouling.

SECTION 7 Cross-flow experiments

Recently, all membranes were tested in a cross-flow cell operated at 1 to 1.8 m/s cross-flow velocity. The results of these tests are as follows;

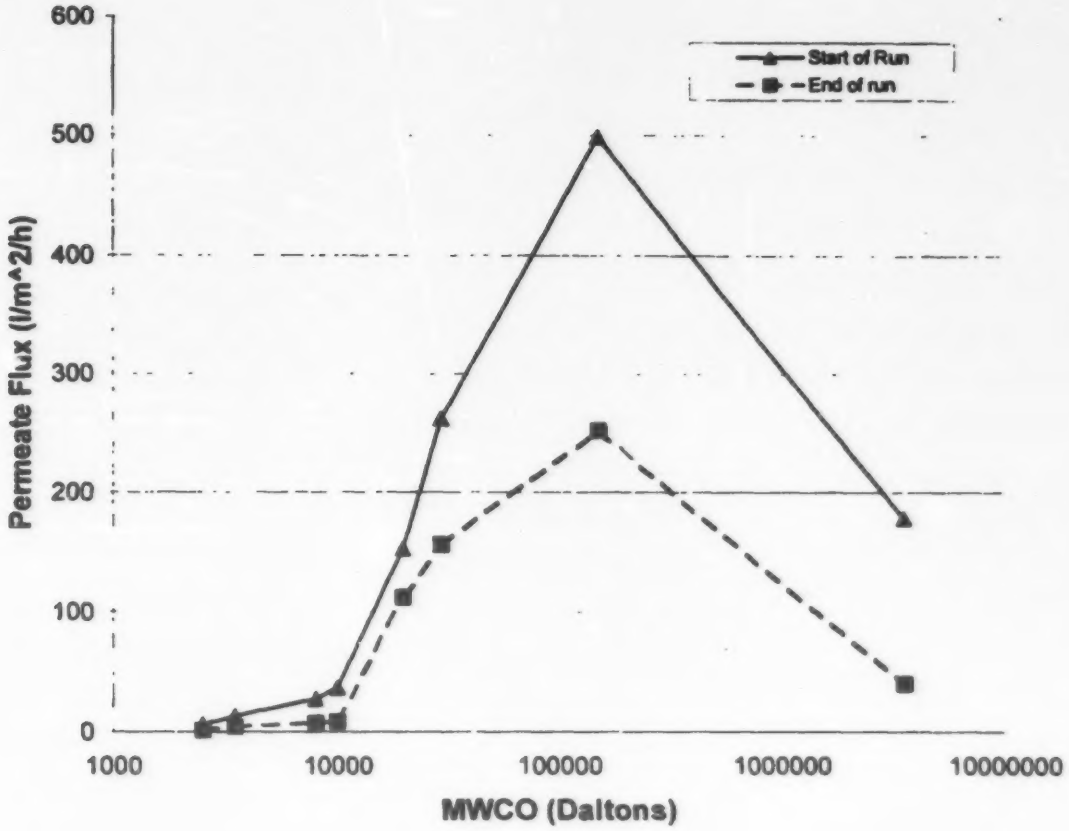

Figure 7.1 Plot of permeate flux at the start and end of a 24 hour run vs. molecular weight cut-off for the membranes listed in Table 1.1 above. Below 100,000 MWCO the runs were performed at 55 and 45 psi and normalized to 50 psi. Above 100,000 MWCO the runs were performed at 32 and 26 psi and normalized to 30 psi. The 50 psi and 30 psi values are plotted.

These results show a substantial drop in flux for the QX membrane (70 nm pore radius) versus that of the P707 membrane (14 nm pore radius). This suggests the entrapment of the 70-100 nm (radius) particles in the QX membrane. Under these circumstances, the best membrane should have a pore radius that is below the lowest measured particle radius 40-70 nm or above the 100 nm particle radius. But the pore radius of the QX membrane falls in the middle of this range, it can be estimated as 70 nm (calculated from the 3,500,000 Dalton MWCO) or 0.01 to 0.1 microns from the Manufacturer's specifications.

SECTION 8 Determination of Solid Particulates in Used Oil

The amount of particulates in used oil was determined by mixing 10 g of used oil with 600 mL of hexane. The mixture was then filtered using several 0.45 micron PVDF filters (VWR-Canlab). The filters were weighed before and after loading with particulates. A total of ten filters were used to prevent pore blinding. Filters were replaced when permeate flow was visually observed to decrease. The content of soot particles > 0.45 microns was determined to be 4.9 % by weight used oil. The filtrate was then passed through a 0.02 micron Anopore ceramic membrane and the amount of particles in the 0.02 to 0.45 micron range determined to be 0.72 % by weight used oil. The total soot content of the used oil was taken as 5.62 % by weight used oil.

SECTION 9

Treatment of bilge water before the UF membrane separator

9.1 INTRODUCTION

A NATO expert workshop on Oily Water Separators was held in September 1999 in Hamilton ON. Of the many points discussed during the workshop, many countries reported on the difficulties associated with pretreatment before oily water separators. These pretreatments were of the form of plate separator, settling tank or a hydrocyclone. These were somewhat effective in separating particulate matter which was always found in considerable amounts in the pre-filter (when present) to the membrane system. Fibers were also reported to be present in bilge water.

The use of relatively small tube UF to enhance mass transfer at the surface of the membrane imposes additional requirements on the type and quality of pretreatment required before the feed stream enters the UF module. This requirement leads to frequent filter replacements which increases maintenance and produces solid wastes which must be stored while at sea.

As previously discussed, used oil is a mixture of oil, water, diesel fuel, detergents, oxidized oils, precipitated metals and particulates. Most solid particulates are formed as a result of coking within the engine. The composition of these particulates can range from tars to solid coke depending on the temperature at which they were formed and the metals present in the oil. Their size can range from a few nanometers to several microns. All of these particulates make up the greater part of the silt found in used oil. Silt in the context of petroleum products is defined as particles measuring less than 5 microns. When the used oil is taken out of an engine, the particles can aggregate to form larger ones. However, the fact that they have been filtered in an engine implies that the building blocks forming the larger particles measure approx. 5 microns or less. In addition to this, many particulates in bilge water originate from outside combustion engines such as rust, dust, deposited soot etc...

The separation methods used as pretreatments to the membrane system are all based on the difference in buoyancy between immiscible oil and water phases. Oil droplets having a s.g. of 0.88 (10W30 @ 15 °C) can be readily separated by these techniques. As the oil particles get smaller, they are more difficult to separate due to decreased settling velocities. If the oil is present in a fine emulsion it cannot be separated since the emulsified oil will remain suspended in solution. If a solid particle having a specific gravity of 1.2 is covered in oil, as it would be if it originated in a diesel engine, then the combined solid-oil particle could have a net specific gravity ranging from 0.88 to 1.2. Some particles would have neutral buoyancy (s.g. ~ 1). For illustration purposes, assuming a spherical particle of s.g. 1.2 is covered by a layer of oil s.g.0.88. If the thickness of the oil layer is equal to ¼ of the diameter of the particle it will have a net specific gravity of 1 or a neutral buoyancy. These particles could exist in the form of aggregates impregnated or surrounded by oil that would not be removed in a parallel plate separator or centrifuge. They could also be particles of soot impregnated with oil. This would most likely be the case for the smaller 89 nm particles as carbon black (soot) readily absorbs oil.

These particles of neutral buoyancy cannot be separated by conventional sedimentation/ centrifugation techniques. It is expected that the amount of neutrally buoyant particles would be quite large in the effluent of a technique separating on the basis of flotation or centrifugation such as a parallel plate separator or a hydrocyclone.

Aggregates could be disrupted on shearing. This would create problems if they are not completely covered by detergent before they enter the membrane module. As they would be very sticky and adhere to the membrane material.

During recent trials aboard H.M.C.S. Athabascan, the pre-filter to the membrane modules was regularly clogged. The OWS on this ship uses a hydrocyclones followed by filtration before the bilge water enters the membrane modules. It was reported during the NATO workshop that when samples of this filtrate were centrifuged, it separated into three fractions. One floated, the other remained suspended and a third readily settled to

the bottom of a centrifuge tube. (D. Veinot, DREA, communicated to the NATO expert workshop in Hamilton).

This accumulation was obtained using a 300 micron bag filter. The hydrocyclone should have separated particles this size. It is proposed that the filter was acting as a coalescer. Fine particles aggregated to a film of oil on the surface of the 300 micron filter. This coalescence permitted the filter to capture fine particles that were much smaller than 300 um. These particles, coated with oil, had limited to neutral buoyancy and were not separated in the hydrocyclone but were coalesced in the bag filter.

These observations are identical to those obtained in recent laboratory experiments where treating bilge water made from used oil, a 100 micron bag filter was installed before a membrane module. The filter readily captured fine particles of silt which had not been removed in the settling stage of the experiment. The flux of the membrane increased as the feed solution was circulated in the batch processing loop. The filter was removed and placed in the feed tank to the membrane. Some of the used oil was eventually released in the feed tank. The flux of the membrane decreased considerably after the filter had been removed.

This leads us to a possible pretreatment for the membrane system. The Navies using the PROSEP technology reported that they had settling as a pretreatment. They used chemical cleaning of the membranes and reported sporadic drastic fouling of the membranes. The membranes needed to be severely cleaned after such events.

The objective of this section was to study the nature of the particles leaving the settling/hydrocyclone pretreatment and the effect of shearing and homogenization on the particulates. This work was aimed at reducing the amount of particulates clogging up the membrane pre-filter. The overall objective being to obtain a shearing method to eliminate the need for a bag filter before the membrane, replacing it with a strainer to remove larger particulates.

The bilge water was tested after circulation in a centrifugal pump discharging to atmospheric pressure for one half hour. It was then allowed to settle for one half hour. This represents the baseline case. Ultrasonic treatment was performed by contacting 50 mL aliquots with an ultrasonic probe for 1 minute. Shearing was tested by circulating the bilge water in a jet pump.

9.2 Experimental

Small samples of bag filters were cut and placed in a loop where 4 litres of bilge water was circulated through the test sample for a period of 24 hours. The pressure drop across the filter and the flow rate were used to determine the change in the resistance of the filter over the 24 hour run.

The possibility of pretreating the bilge water in order that it passes through the bag filter was investigated by comparing two high shear treatments. One using ultrasounds (Dismembranor, Fisher Scientific) and the other using a centrifugal jet pump (Grundfos) to pretreat bilge water that had been circulated for one half hour and settled for one half hour.

9.3 Results

The results of these runs are listed in Tables 9.1 and 9.2 below. As seen in Table 9.1 for the 100 micron nominal pore size the ultrasonic treatment increased the resistance of the filter only marginally compared to the increase observed by the untreated bilge water. This is in good agreement with the microscopic observations of the resulting bilge water where the 1 to 2 micron sized particles had a more rounded appearance after sonication than the original particles. However these differences seemed to disappear when the 5 micron filter was tested. These results suggest a sorption mechanism for the accumulation of particles within the filter. The 5 micron filter was closed and the fibers tightly bound compared to the 100 micron filter which had a very open fluffy network of fibers on its inside surface.

Table 9.1 Filter resistance for the 16 mm (5/8 inch) diameter, 100 and 5 micron pore size samples.

Bilge pretreatment	Nominal Pore diameter of filter (micron)	Diameter of sample (mm)	Resistance (x 10^{-7} m^{-1}) Start	Resistance (x 10^{-7} m^{-1}) after 18 hours	% change in Resistance
Bilge water	100	15.9	0.062	0.133	115.6
Ultrasonic treatment	100	15.9	0.096	0.100	4.5
Bilge water	5	15.9	0.139	0.149	7.5
Bilge with Ultra Sound	5	15.9	0.150	0.160	6.2
Bilge with Ultra Sound	5	15.9	0.136	0.154	13.0

Table 9.2 Filter resistance for the 9.5 mm (3/8 inch) diameter, 50 micron pore size, samples.

Bilge pretreatment	Nominal Pore diameter of filter (micron)	Diameter of sample (mm)	Resistance (x 10^{-7} m^{-1}) Start	Resistance (x 10^{-7} m^{-1}) after 20 hours	% change in Resistance
Bilge Water	50	12.7	0.017	0.024	37.0
Bilge Water with Ultra Sound	50	12.7	0.025	0.026	6.4
Bilge Water sheared in Grundfos jet pump	50	12.7	0.030	0.418	1312.4
Bilge Water sheared in Grundfos jet pump	50	12.7	0.022	0.040	80.5

For the small filter sizes, the increase in resistance was not as pronounced. However, the treatment with the Grundfos pump caused the opposite effect where the resistance of the filter increased substantially after treatment. This indicates the aggregation of particles on shearing in the Grundfos pump. This also implies that excessive pump shear on the bilge water before filtration will cause aggregation that enhances accumulation in the filter media.

9.4 Discussion

On close observation, the polyethylene or polyester bag filters are rated for their nominal cut-off but are not absolute filters. They are produced by the melt blowing and spin bonding techniques. These bag filters have a large amount of loose fibers on the inside of the filter and a smoother surface on the outside. Under a normal operation, the use of an asymmetric filter where the pore size decreases in the direction of flow enhances filter capacity as the particles do not accumulate in a single plane on the surface of the filter. The accumulation of particles in a plane causes tremendous increases in hydrodynamic resistance. As previously discussed in this work, particles found in bilge water produced from used oil have a bimodal distribution with one distribution at 89 nm and another at 1.3 microns. If these particles readily adhere to the fibers in the deep bed filter, they will accumulate and eventually plug the filter.

The usual filter material considerations are different in this type of application as in a standard prefilter situation the filter would be designed to retain all micron sized particles from water. In the present is case, the bilge water contains two populations of particles, one in the 0.07 to 0.1 micron range and another ranging from 0.9 to 2.2 microns as seen in Figure 1.12.

In the semiconductor industry where slurry purification is necessary for Chemical Mechanical Polishing of wafers, the Pall corporation recommends filtration to 30 microns in fumed silica slurries measuring 100-150 nm and 40 microns for alumina measuring 200-300 nm. Smaller pore sizes can also be used; the use of 5 micron filters is reported for silica but these filters must be changed after only one or two weeks of operation. These slurries contain 6-30% solids having a considerable amount of aggregated particles in the > 1.0 micron region. These guidelines represent filter pore size to particle size ratios of 300 to 200 for silica and 200 to 133 for alumina respectively. Filtering these slurries is a careful balance between allowing the passage of smaller particles and the filtering out of large aggregates, dry pieces and other material. If these guidelines were used as a worst case for the selective filtration of large agglomerates and material other

than soot and oil from bilge water, the recommended filter size would be approx. 300 to 400 microns. However, if the pretreatment is to be designed for the Koch membrane where the inside diameter of the lumen measures 1.143 mm as a rule of thumb particle filtration should done to 1/10 of this dimension – i.e. approximately 100 microns. The guidelines for slurries as recommended by Pall would not be met if we had a 100 micron filtration requirement and a 4.4 micron diameter native population of particles, the filter pore size to particulate size ratio would then be 100/4.4 =22.7. It is interesting to note that the presence of the larger particulates, although they do not adversely affect permeate flux, indirectly impose a design limitation on the inside diameter of the lumen to be used in a first stage UF or MF module, it should be no less than 133*4.4*10 = 5.8 or 6 mm (applying the $1/10^{th}$ rule of thumb).

This situation is further exacerbated by the fact that 300 micron bag filters have been reported to be plugging in the present DND system. If the previous guidelines were applied to the selection of a pre-filter for bilge water application; a more open or a different type of prefilter filter should be used.

This situation can be explained by material interactions and the mechanisms involved in deep bed filtration. Hydrophilic nano sized silica and alumina slurries are reasonably stable. Soot impregnated with oil is very hydrophobic and will readily de-phase given proper conditions. If a polyethylene melt-blown filter bag is used as a filter material then a hydrophobic material of very high surface area will be in contact with the solution. This hydrophobic surface facilitates the removal of the particle from solution. The particle readily adheres to the hydrophobic surface and is captured by the filter.

In the present case the oil particle is further rejected from solution as bilge water contains an appreciable amount of dissolved salt. Polyethylene and soot impregnated with oil both have much lower dielectric constants than salty water and as such the movement of the oily particle out of solution to adhere to the polyethylene fibers will be favored over what it would be in fresh water.

Melt-blown polypropylene fibers are widely available to clean up oil spills. Melt blown polypropylene is reported to be "the most cost effective sorbent in terms of performance, versatility and cost in battling environmentally hazardous spills" (Publicity from International Spills Products, CA). Polysorb, melt blown polypropylene (Midwest Filter Corporation, Highwood, IL) is reported to absorb 13-15 times its own weight in petroleum based liquids. Containment Corp. markets a line of melt-blown sorbents consisting of a single layer of polypropylene fibers that can adsorb 20 times their own weight (Containment Corp.)

Such melt blown fibers can be produced as small as 4 microns in diameter. If they can adsorb 20 times their weight they have a void fraction of 20/21= 95%. This is a large void fraction, which implies that the medium has many contact points which favours the entrapment of particles much smaller than the rated pore size.

Although the larger particles were not found to affect the transport through the cake layer these can play a major role in plugging even a 300 micron filter. The principle behind deep bed filtration is to remove particles much smaller than the pore size of the filter by entrapment in the interstices within the medium (Weber J.W., 1972). This will be enhanced if particle-filter material interactions are favorable such as oily soot particles flowing through hydrophobic media.

Entrapment is also favored if a quiescent fluid flows through the media. Lower velocities will tend to transform the melt-blown medium into a sorbent bed rather than a filter. So oversizing the prefilter in this case can accentuate the problem.

As a consequence, any filter working on the deep bed principle placed before the membrane system cannot be seen as pretreatment but as an element of the separation process itself. That is any prefiltration will remove particles that should be retained and disposed of in the UF concentrate.

So having a deep bed filter of any size before the membrane transforms it into a separator where the filter will recover a substantial amount of particles. This implies that in a 2000 mg/L oil mixture containing 40 % used oil, the >0.45 micron particulate content is 2000*0.4*0.049 = 39.2 mg/L. At 2 GPM for a 3 in diam. by 10 in long filter, should all the particles be retained in one plane, the filter will receive monolayer coverage in 8 hours. This indicates that the filter will be quite challenged for a 30 day operation if the 4.4 micron diameter particles are retained by the filter. The results of this calculation only include micron sized particles in the used oil portion of the bilge water. As seen in Figures 1.2 and 1.3 the 1 micron plus particles should readily accumulate in the cake and will not contribute to cake resistance in the presence of smaller particles as the specific cake resistance, define by Equation 5, is inversely proportional to the square of the particle radius.

Conclusions

Ultrasonic treatment increased the resistance of the filter only marginally compared to the increase observed with the untreated bilge water. This was attributed to the more rounded shape of 2 to 4 micron sized particles found in sonicated bilge water. These differences disappeared when the 5 micron filter was tested suggesting that sorption and depth filtration play a role in the accumulation of particles within the 100 micron filter.

Treatment with the Grundfos pump caused the opposite effect where the resistance of the filter increased substantially due to treatment. This suggests that particles are aggregating on shearing in the Grundfos pump. This also implies that excessive pump shear on the bilge water before filtration will cause aggregation that enhances accumulation in the filter media.

The results suggest the use of a filtration medium that will not act as a deep bed filter. They also indicate that modules having larger lumen sizes be tested to remove the particulate retention load on the pretreatment step (dead-ended filtration) and move it to the cross-flow filtration where the micron sized particles can be removed and disposed of in the concentrate stream.

SECTION 10 Pilot Scale Studies

The flat sheet tests described above, provided an understanding of the effects of bilge water particulates on permeate flux. With this understanding of bilge water characteristics it was then appropriate to simulate actual shipborne conditions through the use of pilot scale testing. This allowed for operational parameters, such as backflushing, to be examined. Backflushing is expected to enhance membrane flux by reducing cake layer resistance and membrane fouling.

Pilot scale tests were performed using the synthetic bilge water mixture described in section 1.5. Two modules were tested, a ceramic membrane CERAMEM (Waltham, Massachusetts, USA) LMA-0005-PS and a polyacrylonitrile (PAN) KOCH (Ann Arbor, Michigan, USA) CM polymeric membrane.

10.1 Experimental

Membrane modules were tested in the pilot scale set-up as detailed in Figure 10.1. The flows through the system are depicted as follows; routine flow of bilge water and permeate is depicted by the bold flow line; hashed flow line depicts backflushing; and light flow lines depict membrane by-pass or over pressure release safety line. This pilot plant system consisted of a 200L tank providing feed for a rotary vane pump (PROCON, Murfreesboro, Tennessee, USA), which in turn fed the membrane module. A backpressure valve, mounted after the membrane module, maintained the system's operating pressure. This valve was pneumatically operated and computer controlled. This provided an extremely fine pressure control, within 0.7KPa (0.1psi) over 24 hours. The trans-membrane pressure was normally at 206KPa gauge (30psig). However, for certain runs conducted at higher cross-flow velocities the lowest system pressure attainable was 220KPa gauge (32psig). All experimental data was corrected to 206KPa gauge (30psig) as per ASTM standard D5090-90: Standardizing Ultrafiltration Permeate Flow Performance.

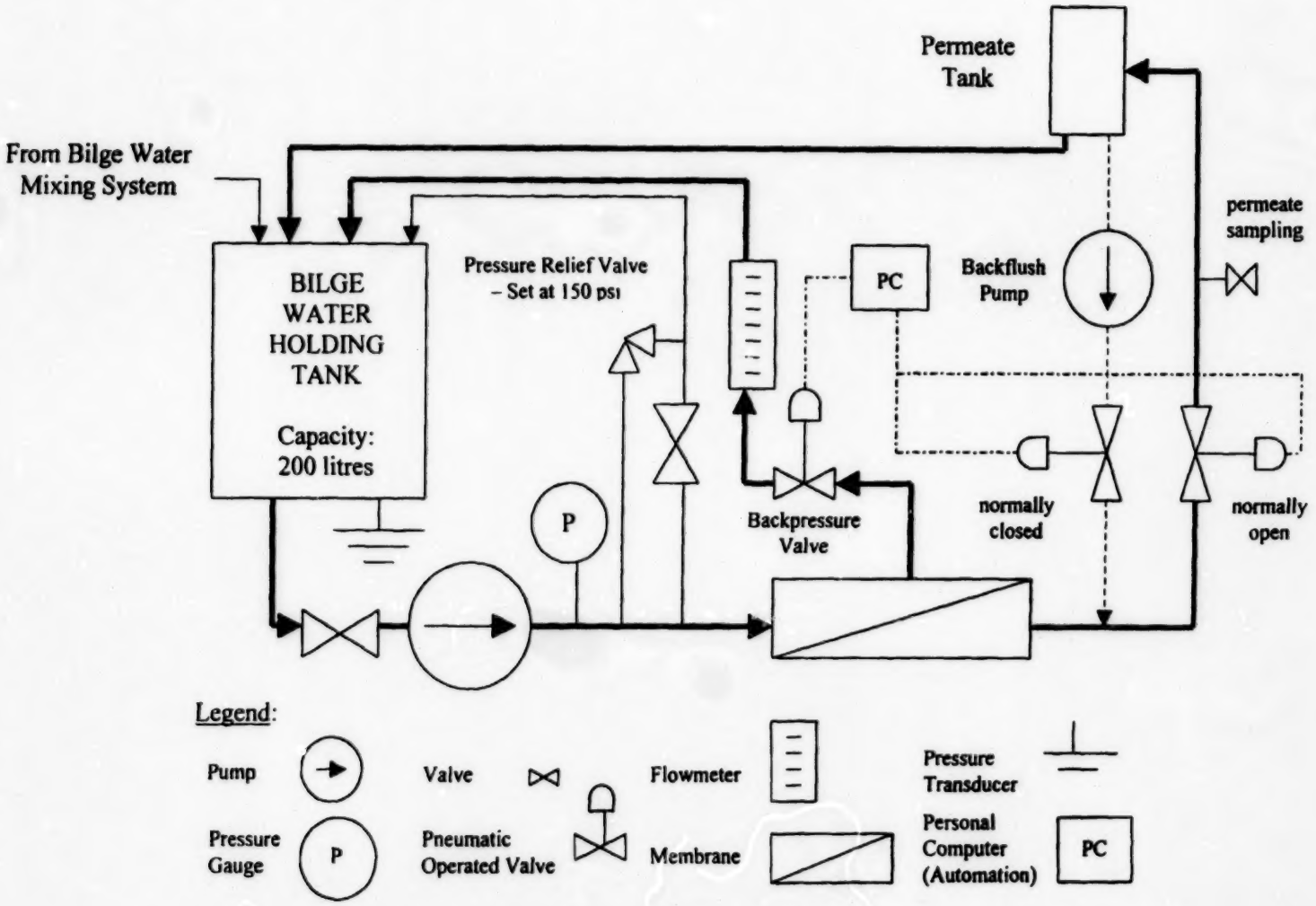

Figure 10.1: Pilot Scale Experimental Set-up

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The temperature of the bilge water was controlled to 25°C. The initial bilge water temperature was approximately 23°C and was heated up to this temperature by means of the thermal energy imparted by the system's main pump. To ensure the bilge water temperature did not exceed 25°C a cooling coil, supplied with cold tap water, was inserted in the bilge water holding tank. The passage of cold water through the cooling coil was controlled by a computer controlling a pneumatic valve. Once the bilge water warmed to the 25°C temperature set point the system was able to maintain the temperature of the bilge water to within plus or minus 0.1°C. The flux values for the data obtained in the earlier portions of the experimental runs, when the bilge water had not achieved a temperature of 25°C, were corrected to 25°C as per ASTM standard D5090-90: Standardizing Ultrafiltration Permeate Flow Performance.

The system also provided backflushing to the membrane module, using a pneumatic diaphragm pump. This pump drew a suction from the permeate tank shown in Figure 10.1. The backflushing pressure was maintained at 241KPa gauge (35psig). While the backflush pump was constantly operated at 241KPa the backflushing of permeate to the membrane was controlled by means of a valve located between the diaphragm pump and the membrane module. This valve was normally in the closed position; i.e. it ensured no backflushing of permeate through the membrane. During the backflushing operation the valve was opened and permeate was backflushed through the membrane. This valve was operated in conjunction with the valve between the membrane module and the permeate tank which was normally open and closed during backflushing operation; thus ensuring the flow of permeate through the membrane. The total operational cycle and the backflushing times were computer controlled. The permeate flux from the membranes was determined by measuring the liquid level in the permeate tank. This provided a time averaged value of the permeate flux representing the actual membrane throughput over the course of the run.

After every experimental run the membrane module was removed from the pilot scale system and cleaned. The membranes were cleaned with a detergent specifically formulated to regenerate membranes fouled during oily wastewater treatment processes.

The detergent was purchased from KOCH Membrane Systems Incorporated (Ann Arbor, Michigan, USA) and under the commercial name of KLD II – KOCH KLEEN. KLD II is a strongly basic cleaner, however its exact formulation is not known due to its proprietary nature. (A 1 percent solution of KLD II has a pH ranging from 10 to 11.5.) The membrane regeneration procedure was to wash the membranes with a water-KLD II solution. The concentration of the KLD II in the wash water was 5 mL/L of water. Additionally, the water was heated in order to enhance the cleaning action. For the polymeric membrane the cleaning solution was heated to 40°C ± 2°C and used for approximately 30 minutes or when the temperature of the cleaning solution dropped to below 30°C. For the ceramic membrane the cleaning solution was heated to 65°C ± 5°C and used for approximately 45 minutes or when the temperature of the cleaning solution dropped to below 40°C. These washes were conducted at high cross-flow velocities (in excess of the operational cross-flow velocities) and low pressures (between 3 to 5 psi). For either membrane numerous cleaning cycles were conducted in order to regenerate (as best as possible) the membrane to its original conditions, with a minimum of three cleaning cycles being conducted per membrane.

Pressure, temperature, operational cycle time and backflushing time were controlled using LABVIEW (National Instruments) software. The main feed pump's speed was manually controlled and operated at approximately 60% capacity.

The following membrane modules were tested in the pilot plant experimental set-up:

a. CERAMEM (Waltham, Massachusetts, USA) LMA-0005-PS ceramic membrane (from this point on referred to as the CERAMEM LMA membrane):

Material:	silica selective layer on an alumina substructure,
Membrane Selectivity:	pore radius of 0.0025 microns
Membrane Configuration:	tubular,
Membrane Dimensions:	length of 0.325m, 2mm square flow channel; and

b. KOCH (Ann Arbor, Michigan, USA) CM polymeric membrane (from this point on referred to as the KOCH CM membrane):

Material:	polyacrylonitrile
Membrane Selectivity:	MWCO of 50,000 Daltons
Membrane Configuration:	small tube UF,
Membrane Dimensions:	length of 0.417m,
	fibre diameter of 1.143mm.

The cross-flow velocities used in the experimental runs were dependent upon the membrane module used. The cross-flow velocity used for the CERAMEM LMA membrane ranged from 1.04 m/s (15 L/min) to 1.74 m/s (25 L/min). For the KOCH CM membrane the cross-flow velocity ranged from 3.12 m/s (12.5 L/min) to 3.75 m/s (15 L/min). These ranges of cross-flow velocity were necessary in order to operate both modules under similar trans-membrane pressure conditions.

The majority of the experimental runs were conducted at a trans-membrane pressure of 207.6 KPa (30 psig). Runs treating bilge water, consisting of new diesel engine lubricating oil ("new bilge water"), using the CERAMEM LMA membrane and using a cross-flow velocity of 1.74 m/s were performed at 221.4 KPa (32 psig); this was the lowest pressure achievable using this cross-flow velocity. For all experimental runs the temperature normally started near 23°C and increased to 25°C due to the thermal energy imparted by the system's pump. In accordance with the ASTM standard D5090-90: Standardizing Ultrafiltration Permeate Flow Performance all of the experimental data presented in this section has been corrected to a trans-membrane pressure of 207.6 KPa (30 psig) and a temperature of 25°C.

10.2 Pilot Scale Testing Results

Examination of the various membrane modules, particularly following experimental runs with used bilge water, revealed a slight build up of material at the entrance of the membrane flow channels. Prior to the experimental runs with the KOCH CM membrane and the treatment of bilge water made with used diesel engine lubricating oil ("used bilge water"; this was the final set of experimental runs), a pre-filter was added to the system.

The purpose of this pre-filter was to safeguard against the possibility of plugging at the entrance of the membrane's hollow fibres. This pre-filter appears to have coalesced oil as the bilge water was circulated through the system. The impact of this pre-filter was noted prior to the non-backflushed run. For this run the pre-filter was not only removed, but the bilge water retentate was run through it in an attempt to reverse any pre-filtration effects caused by it. Due to the different conditions that this series of experimental runs were conducted under they will be addressed separately.

10.2.1 Flux Decline Due to Irreversible Fouling

Prior to the examination of the experimental data it is worthwhile to examine the effects of fouling on the membrane modules. Irreversible fouling results in the degradation of a membrane's flux capacity and therefore must be identified and corrected for in order to properly compare experimental data.

Ideally the best method to evaluate the irreversible fouling would be to clean and conduct pure water permeate runs after each experimental run. While the membranes were cleaned following each run, batches of synthetic bilge water were used for multiple runs, due to the length of time required to make up synthetic bilge water. Until a batch of synthetic bilge water was disposed of it was not possible to conduct a pure water permeate run. Accordingly, pure water permeate runs were not conducted following each run. However, the extent of irreversible fouling could also be identified by the degree of flux decline from run to run.

The degree of irreversible fouling was determined by examining the very early bilge water flux of each experimental run – i.e. within the first 1 to 5 minutes – and noting the overall decline, if any, in these values. While these early bilge water flux values are not expected to precisely simulate pure water permeate flux values it is reasonable to expect these values to closely approximate the decline in pure water permeate flux after a sequence of experimental runs. Figures 10.2 and 10.3 show these initial flux for the CERAMEM LMA and KOCH CM membrane modules, respectively. These figures are

comprised of data from both new and used bilge water runs and are presented versus the sequence (i.e. the chronological order) in which the experimental runs were conducted.

For the CERAMEM LMA membrane the pure water permeate flux value, before and after the sequence of runs, was approximately 97.1 L/m^2/hour and 64.7 L/m^2/hour, respectively. As revealed by Figure 10.2 the CERAMEM LMA membrane experienced a continual flux decline over the course of the experimental runs, caused by the inability of the cleaning regime to completely remove all the fouling which built up on the membrane surface during bilge water treatment. Accordingly, the CERAMEM LMA membrane flux results need to be corrected for this continual flux decline due to the increasing membrane resistance as the runs proceeded. Based upon the slope of the best fit for these bilge water values, identified in Figure 10.2, the CERAMEM LMA membrane experienced a flux decline of approximately 1.68 L/m^2/hour for each experimental run. Due to the irreversible fouling, experienced by the CERAMEM LMA membrane, the direct comparison of flux data from one experimental run to another does not solely represent the impact of the individual parameters examined. To mitigate the impact of the CERAMEM LMA membrane's fouling and therefore to properly compare the CERAMEM LMA membrane's experimental runs flux ratios, rather than the fluxes, were examined. The flux ratio is defined as:

$$\text{Flux Ratio} = \frac{\text{Bilge Water Flux}}{\text{Estimated PWP Flux for the given Bilge Water Run}} \qquad (10.2)$$

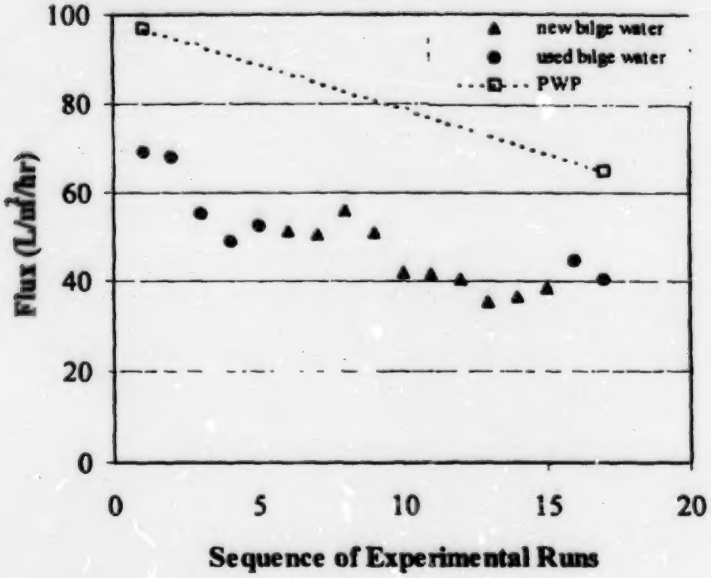

Figure 10.2: CERAMEM LMA Membrane Flux Decline

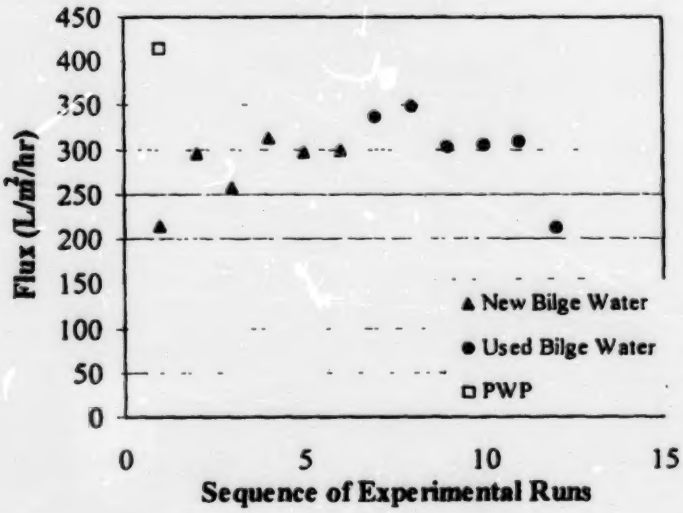

Figure 10.3: KOCH CM Membrane Flux Decline

For the KOCH CM membrane the pure water permeate flux for the new "as received" membrane was approximately 415 L/m^2/hour. Unfortunately, a post bilge water pure water permeate flux was not obtained, as the KOCH CM membrane experienced a catastrophic failure at the end of its experimental runs; the membrane ruptured as witnessed by the presence of oil on the permeate side of the membrane. The KOCH CM membrane had a transparent plastic housing allowing for this observation. As evidenced by Figure 10.3 the initial bilge water flux for the KOCH CM membrane did not appear to experience any irreversible fouling. Therefore the flux, from these various experimental runs, were compared directly for the KOCH CM membrane.

10.2.2 Estimating the Experimental Error in the Pilot Scale Flux Measurement.

In order to properly assess the various experimental results it is necessary to determine if differences in observed flux are due to the changes in operational parameters or error. To assess the error it is necessary to review similar runs. However, due to the length of the experimental runs, their duration was 1 to 3 days, it was not possible to conduct many duplicate runs. Additionally, due to fouling (particularly for the CERAMEM LMA membrane) it is very difficult to obtain duplicate runs.

However, the error associated with a given experimental run can be identified once the steady state conditions have been achieved. At the steady state conditions the cake layer thickness is constant and therefore the flux should stabilize and thus the flux data, after this time, are essentially duplicate runs. The best runs to examine error are those that did not use any backflushing; as the reason for backflushing is to ensure that the cake layer does not reach its maximum thickness.

Accordingly, the experimental runs, for the CERAMEM LMA membrane, with no backflushing, were examined in order to determine the error, or precision, associated with the experimental runs. Various experimental runs, conducted with no backflushing were examined for the error associated with the flux, after the system had achieved steady state conditions; i.e. the cake layer had achieved its steady state thickness. All of the runs had

very similar error associated with the steady state flux. Figure 10.4 presents the flux data for the CERAMEM LMA membrane, with no backflushing, a trans-membrane pressure of 220KPa gauge and a cross-flow velocity of 1.74m/s. As seen from Figure 10.4 the flux appears to achieve a steady state value after approximately 31.5 hours of operation. The solid line is the average steady state flux. The dashed lines indicate the 95% confidence interval for the steady state flux. The average steady state flux was approximately 38.52 ± 0.24 L/m^2/hour. This error equates to a percent error of approximately 0.63%. This error will be used throughout the analysis of the experimental data.

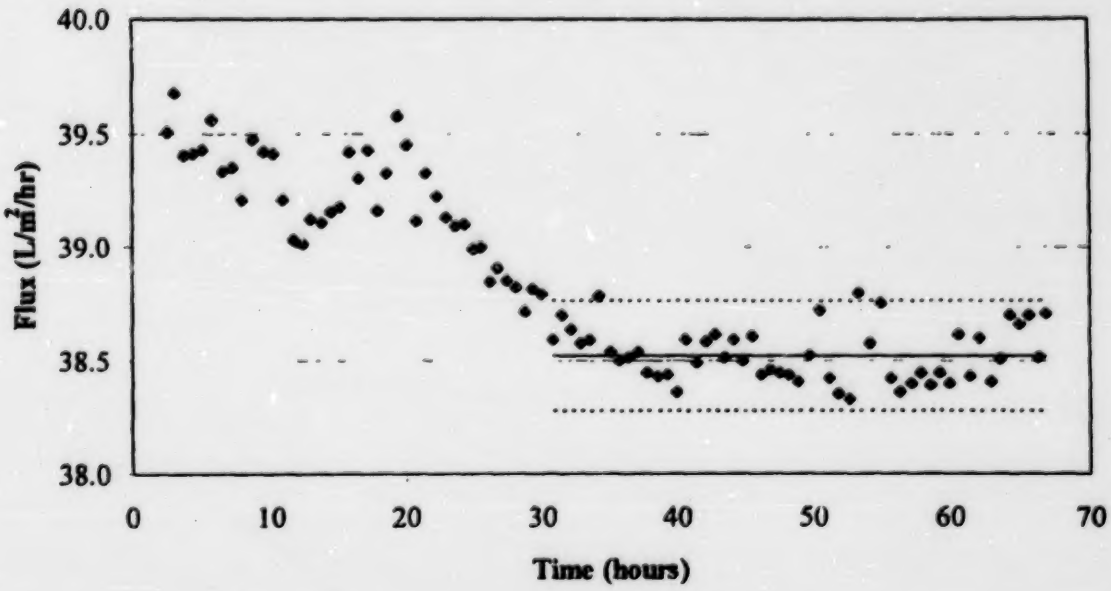

Figure 10.4: CERAMEM LMA Membrane, No Backflush, Operational Pressure of 220KPa, Cross-Flow Velocity of 1.74 m/s

Flux ratio (equation 10.2) will have a greater error associated with it than will the flux, since it utilizes flux in both the numerator and denominator of its equation. Accordingly, the percentage error associated with the use of flux ratio will be:

$$Flux\ Ratio = \frac{Flux \pm 0.63\%}{PWP\ Flux \pm 0.63\%}$$

equating to an error of ± 1.26%.

10.2.3 Effect of Bilge Water Composition

For the KOCH CM membrane, experimental runs conducted with used bilge water were performed with a membrane pre-filter, while experimental runs conducted with new bilge water did not have this pre-filter. Therefore these two sets of experimental runs cannot be compared. Therefore to identify the impact of new versus used bilge water on flux the various CERAMEM LMA membrane experimental runs were compared. Figures 10.5 through 10.7 are the experimental results for the CERAMEM LMA membranes, comparing new and used bilge water runs with comparable operational parameters – i.e. the same backflush and cross-flow velocity and using flux ratio to account for flux decline and any trans-membrane pressure differences.

As shown in the previous section, the treatment of new or used bilge water appeared to be immaterial with respect to the irreversible fouling associated with the membranes. However, as seen with the flat sheet testing, new and used bilge water did result in different flux values, likely caused a different cake layer formation (be it differing emulsion sizes within the cake layer or differing cake layer thickness). Figures 10.5 and 10.6 reveal a higher flux ratio (and therefore a higher flux) for new bilge water as compared to used bilge water, corroborating the flat sheet results. However, the magnitude of this difference, for the CERAMEM LMA membrane module, is not as great as that observed with the flat sheets. This is likely the result of the fact that the shear rate at the surface of the membrane in the stir cell was much lower, resulting in a thicker cake and therefore a greater cake layer resistance. Associated with a greater cake layer resistance would be an increased observation of its impacts and thus an increased

difference between new and used bilge water. Additionally, the experimental runs using flat sheet membranes were operated at higher trans-membrane pressures and therefore they would experience a greater cake layer resistance than the pilot scale modules.

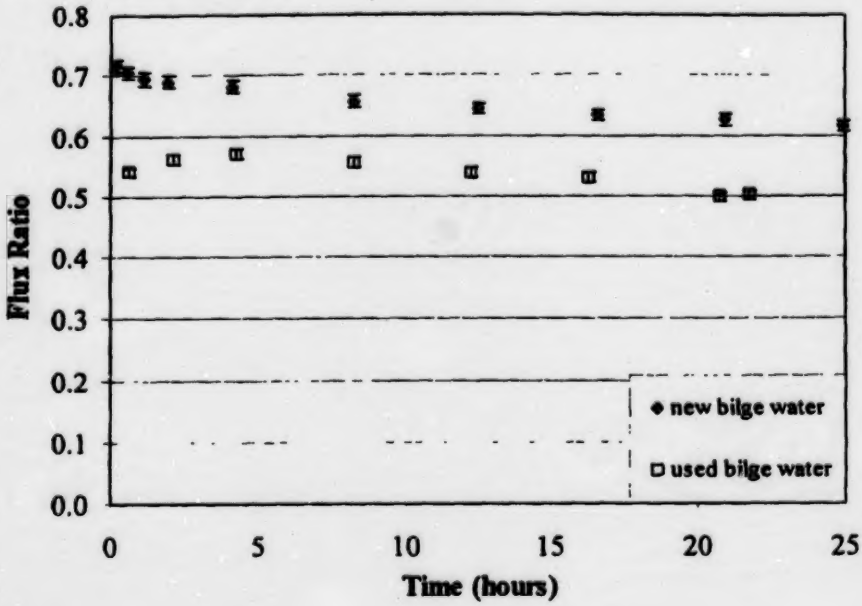

Figure 10.5: CERAMEM LMA Membrane –2.5 second Backflush per 120 second cycle

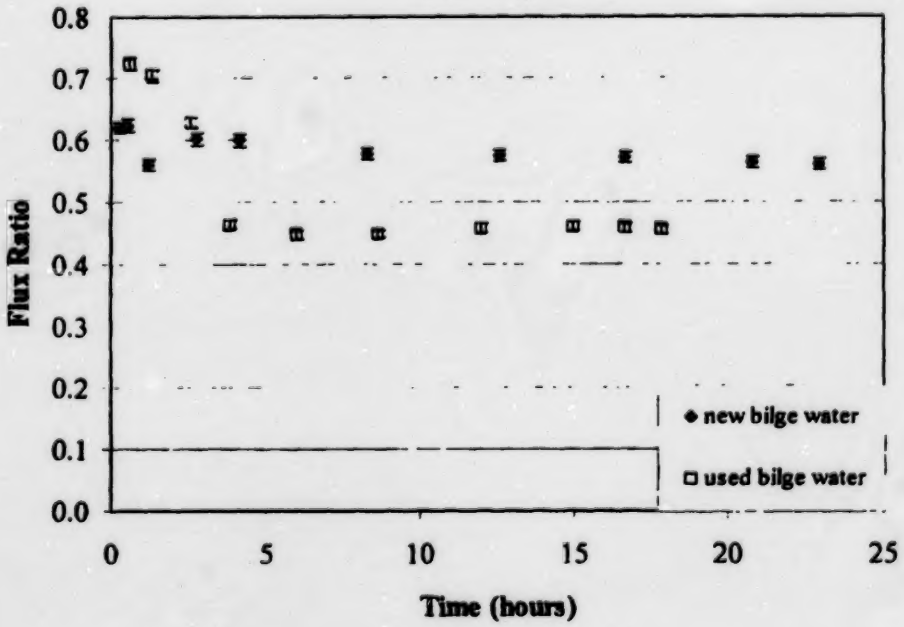

Figure 10.6: CERAMEM LMA Membrane –5 second Backflush per 120 second cycle

10.2.4 Effect of Backflushing

While Figures 10.5 and 10.6 demonstrate the fact that bilge water, consisting of used lubricating oil, is more difficult to treat than bilge water, consisting of new lubricating oil, examination of varying degree of backflushing shows that the difficulty associated with used bilge water can be mitigated. Figure 10.7, compares new and used bilge water runs, for the greatest degree of backflushing conducted during experimental testing; a 10 second backflush in a 120 second total cycle time. It shows virtually no difference in flux for new and used bilge water runs. A closer review of Figures 10.5 and 10.6 shows that a greater degree of backflushing, 2.5/120 versus 5/120, is accompanied by a greater difference between the new and used bilge water fluxes. For the 2.5 second backflush (Figure 10.5) the difference in flux ratios between the new and used bilge water runs was approximately by 0.113, after approximately 24 hours of operation.

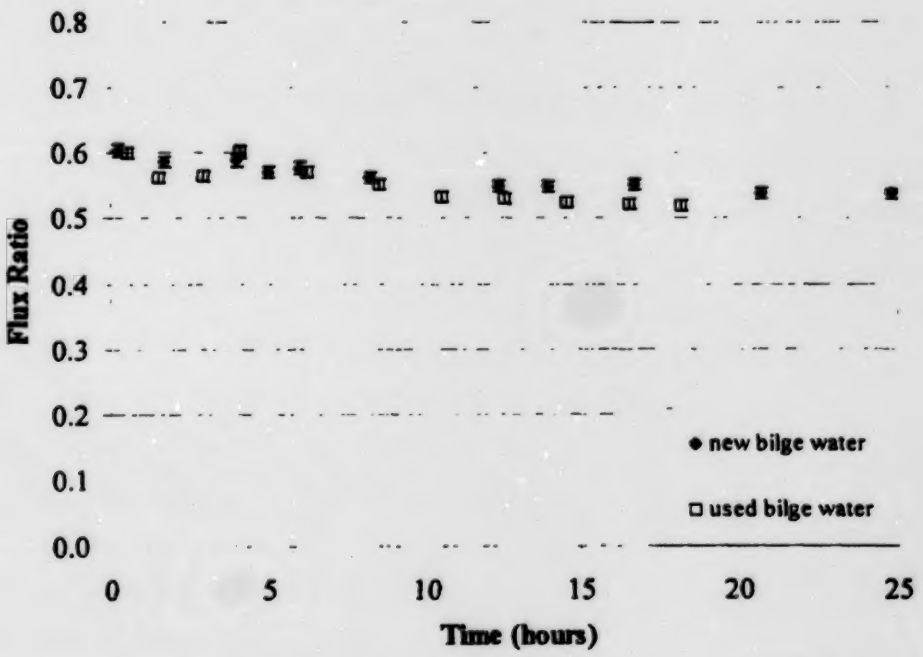

Figure 10.7: CERAMEM LMA Membrane –10 second Backflush per 120 second cycle

Whereas for the 5 second backflush (Figure 10.6) the difference in flux ratios was approximately 0.104. Again, Figure 10.7 shows no flux difference when the backflush is increased to 10 seconds. Therefore it appears that increasing backflushing lessens the negative impact of used bilge water. Whether the negative impact of the used bilge water cake layer is due to better adhesion to the membrane or a thicker layer or another factor, it seems that a greater backflush duration more effectively removes this cake layer.

Figures 10.8 and 10.10 provide a comprehensive examination of the all the experimental runs conducted with varying degrees of backflushing, for the CERAMEM LMA and KOCH CM membranes respectively. (These figures show experimental runs conducted for the treatment of bilge water composed with new lube oil.) From these figures the positive impact of backflushing, albeit small, can be noted. Figures 10.9 and 10.11 are provided to identify the error associated with the various experimental runs; in order to clearly show the error only selected data from Figures 10.8 are presented.

For the CERAMEM LMA membrane Figure 10.8 displays the experimental results in terms of flux ratio versus time, rather than flux versus time, due to the irreversible fouling that it experienced. To categorically confirm the positive impact associated with backflushing, for the CERAMEM LMA, Figure 10.12 displays the flux versus time results.

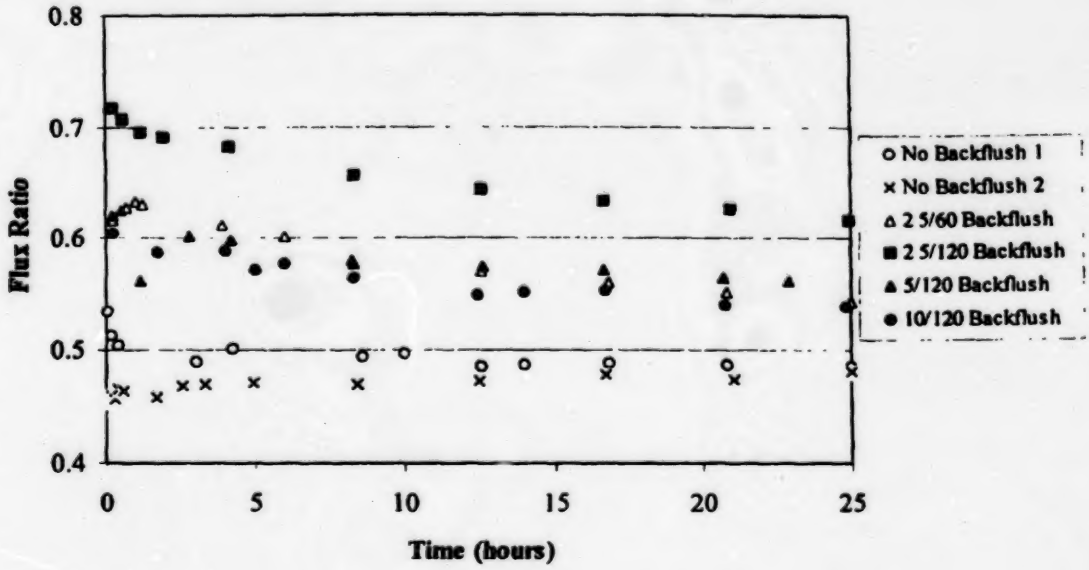

Figure 10.8: CERAMEM LMA Membrane Treating New Bilge Water with Varying Degrees of Backflushing – at 220 KPa

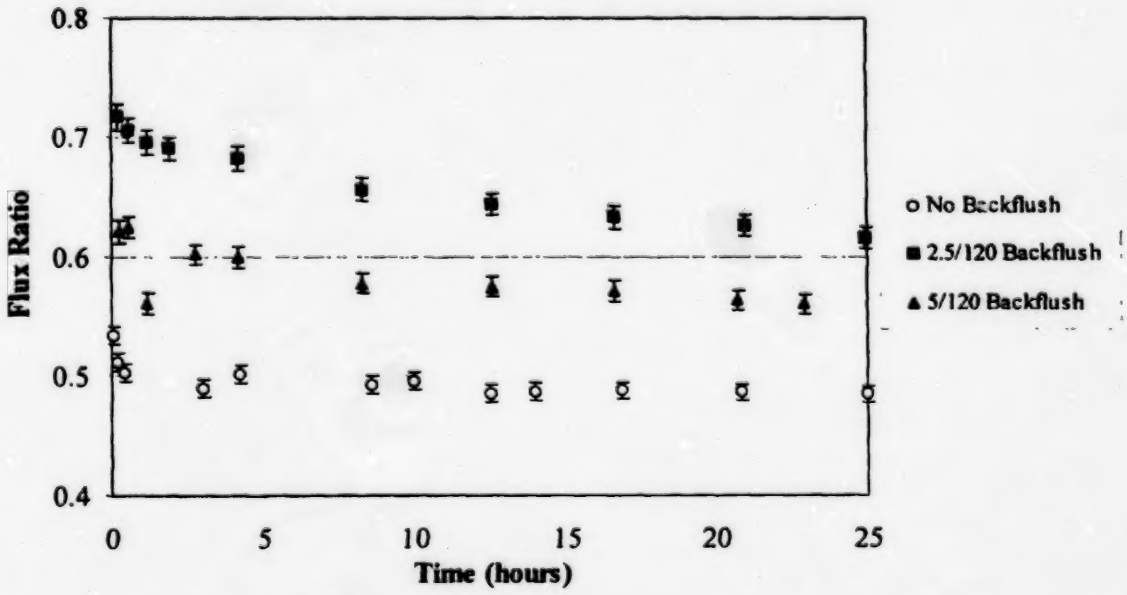

Figure 10.9: CERAMEM LMA Membrane, selected runs including error bars, New Bilge Water Experimental Runs

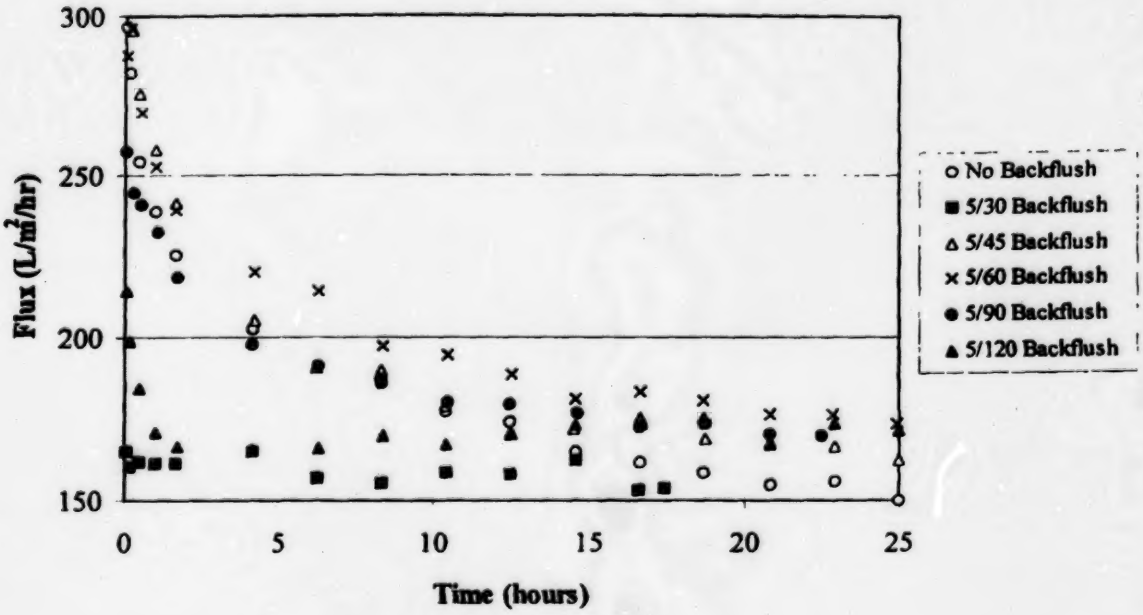

Figure 10.10: KOCH CM Membrane Treating New Oil Bilge Water with Varying Degrees of Backflushing – at 206 KPa

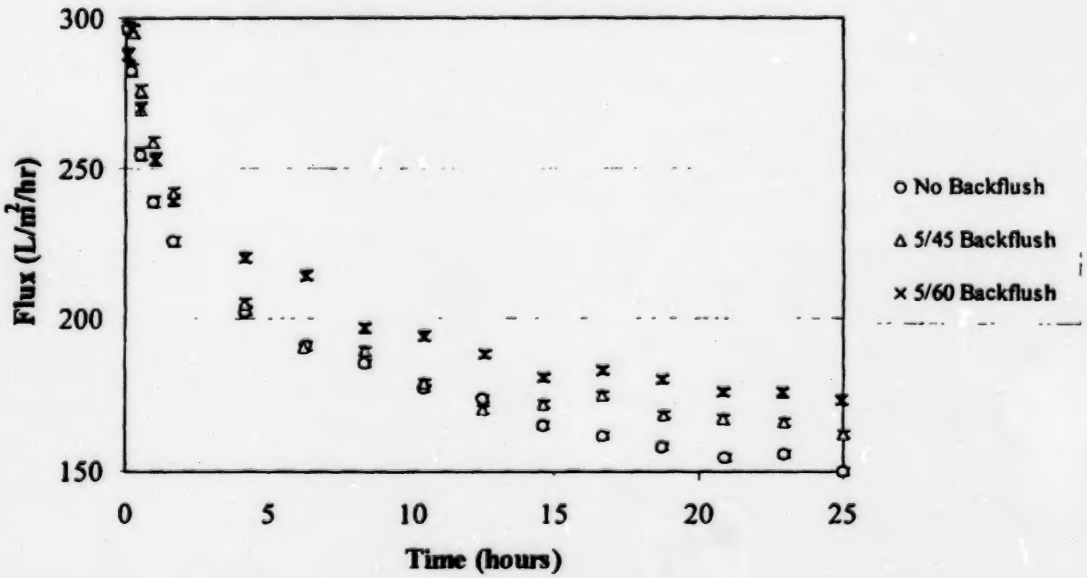

Figure 10.11: KOCH CM Membrane, selected runs including error bars, New Bilge Water Experimental Runs

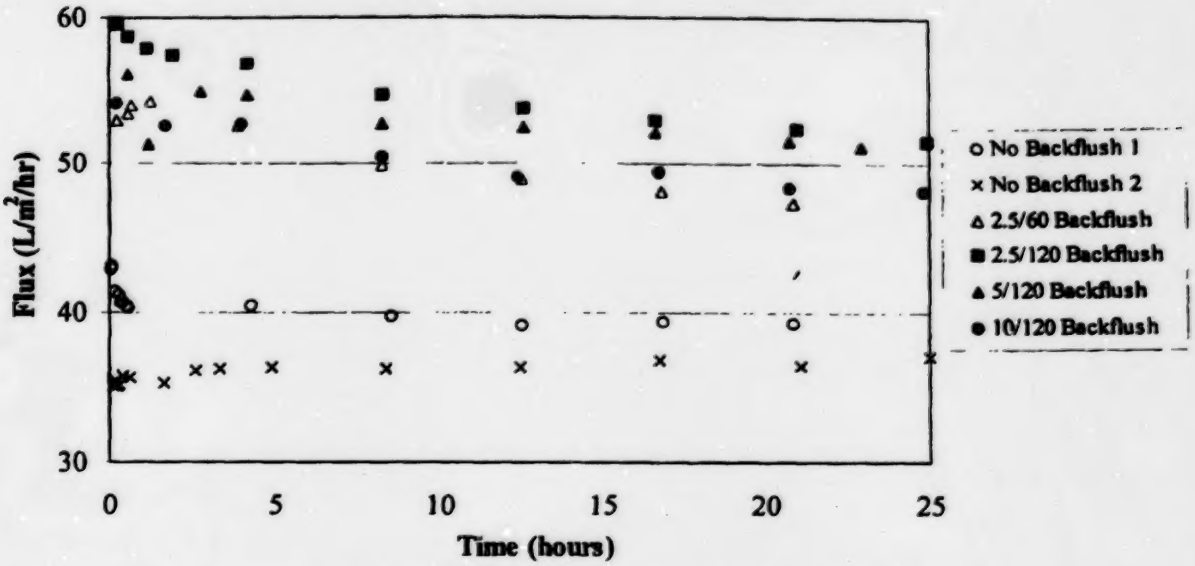

Figure: 10.12: CERAMEM LMA Membrane Treating New Bilge Water with Varying Degrees of Backflushing – at 220 KPa

For the CERAMEM LMA membrane backflushing improved the permeate flux ratio by up to 27%, based upon the flux at 24 hours. The actual permeate flux went from 40 $L/m^2/hr$ for the run without backflushing to 54 $L/m^2/hr$ for the run with the 2.5 second backflush. This is an improvement of 35%, which translates to an equivalent reduction in the required membrane surface area. The maximum observed flux enhancement resulted with a backflush of 2.5 second in a 120 second cycle time, the smallest backflush applied to the CERAMEM LMA membrane. The remaining backflushes, while providing an improvement over the non-backflushed runs, provided approximately the same improvement. Therefore, for the CERAMEM LMA membrane, it appears that the initial backflushing force provides the majority of benefits with any additional benefits being offset against the time lost when permeate is not produced.

While the impact of backflushing is not as apparent for the KOCH CM membrane, it still provides some minor flux enhancement, with the exception of the 5 second backflush in a 30 second total cycle time. Backflushing after this shorter period may not have been

effective as permeate is used to perform this operation. The 5 seconds over a total time of 30 seconds could have negated the benefits associated with the cake layer reduction.

To evaluate the effectiveness of backflushing it is necessary to review the non-backflushed runs in order to identify a benchmark to compare backflushed runs against. These runs will allow for an estimation of the time required for the cake layer to achieve its steady state conditions. As described in section 1.4.3 the steady state time can be determined through the use of equation 17. Therefore to solve for the steady state time the membrane's pure water permeate flux, the steady state flux when treating bilge water and the flux decline constant (τ_c) are required. The pure water permeate flux and the steady state flux, when treating bilge water, are readily apparent from the experimental data. The value of the steady state flux ($J(t_{ss})$) is taken as being the flux after 24 hours of operation. This value is used as it is very likely that the cake layer will have achieved steady state conditions by this time.

As defined in equation 16 the flux decline constant (τ_c) is a function of the membrane resistance, maximum and bulk solute volume fractions, pure water permeate flux and specific cake layer resistance, of which only the specific cake layer resistance is not known. The specific cake layer resistance is determined through equation 5, which is dependent upon the maximum solute volume fraction and the critical solute size. For the CERAMEM LMA and KOCH CM membranes the critical solute particles radii are 0.047 microns and 0.042 microns, respectively.

The steady state cake layer thickness can be determined through equations 4 or 15. (If equation 4 is used, the cake layer resistance can be determined from the experimental data.) Therefore, for the treatment of new oil bilge water, the steady state conditions for the CERAMEM LMA and KOCH CM membranes are estimated as follows;

	Steady state time	Cake Layer Thickness
CERAMEM LMA	6 hours	155 microns
KOCH CM	20 minutes	36.8 microns

The greater cake layer thickness, associated with the CERAMEM LMA membrane, could explain why the CERAMEM LMA membrane is more affected by backflushing. Since the CERAMEM LMA membrane has an increased cake layer thickness it experiences greater cake layer resistance and therefore backflushing does provide some benefit.

Figure 10.13 details the theoretical fit for the CERAMEM LMA membrane, with no backflushing. Figure 10.14 reveals the fit for the KOCH CM membrane, again without the use of backflushing. The shorter steady state time and thinner cake layer, achieved by the KOCH CM membrane, can be better understood when examining the impact of cross-flow velocity on both membranes. The CERAMEM LMA membrane was operated with a cross-flow velocity of 1.74 m/s, the maximum velocity allowing for a pressure of 30 or 32 psi. However, the KOCH CM membrane was operated with a cross-flow velocity of 3.75 m/s. This resulted in the CERAMEM LMA membrane being operated under laminar conditions (a Reynolds number of approximately 1900) while the KOCH CM membrane was operated under turbulent conditions (a Reynolds number of approximately 4800). The difference between laminar and turbulent flow is known to have a significant impact upon the cake layer conditions as turbulent conditions are known to result in reduced cake layer thickness (Koltuniewicz et al., 1995). Similarly, Porter identified that the mass transfer co-efficient, and thus membrane flux, has a greater dependence on cross-flow velocity in turbulent flow as compared to laminar flow. In turbulent flow the mass transfer co-efficient is proportional to the cross-flow velocity raised to the power of 0.8 compared to the power of 0.33 in laminar flow (Porter, 1990).

From Figures 10.13 and 10.14 it can be observed that the theory overpredicts the (initial) flux for the CERAMEM LMA membrane and underpredicts flux for the KOCH CM membrane. An important limitation of the theory is that it does not incorporate fouling effects into its determination of flux. Therefore the overprediction for the CERAMEM LMA membrane suggests that the CERAMEM LMA membrane experiences fouling very early in its exposure to bilge water, whereas the KOCH CM membrane may be much more tolerant to the bilge water and fouls more gradually.

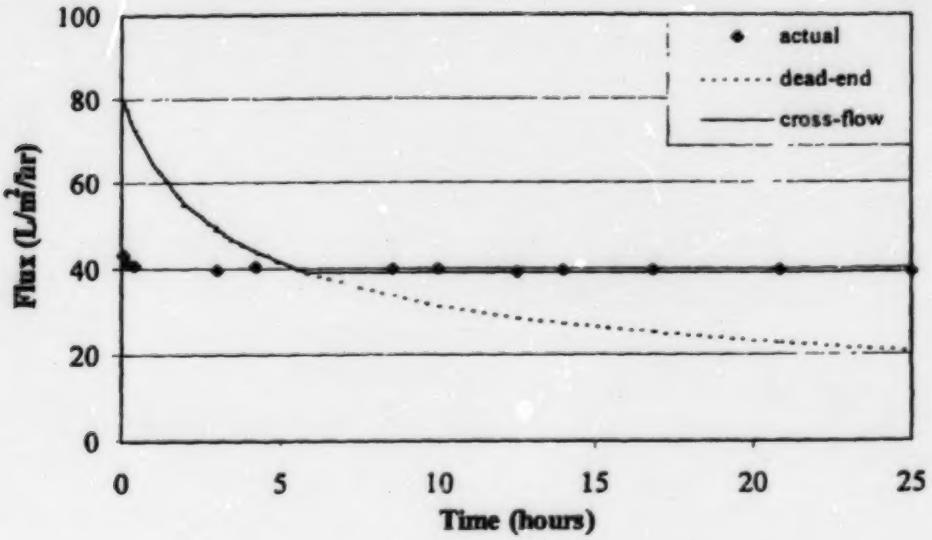

Figure 10.13: CERAMEM LMA Membrane Treating New Oil Bilge Water at 220 KPa with No Backflush

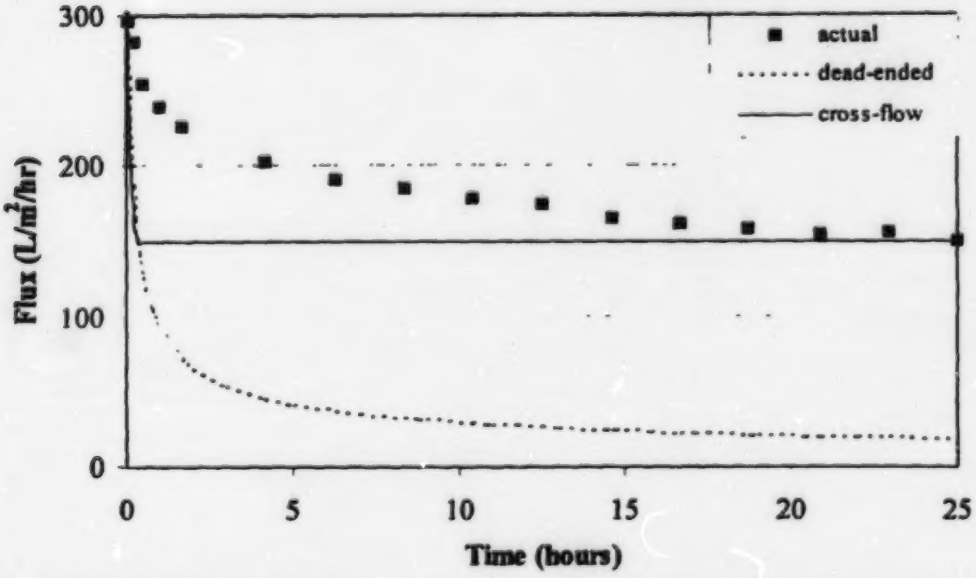

Figure 10.14: KOCH CM Membrane Treating New Oil Bilge Water at 206KPa with No Backflush

To assess the impact of backflushing it is necessary to determine if the cake layer produced, during normal operation, is removed during backflushing. This was done by incorporating a term in equation 12 that accounts for cake removal after each backflusing cycle. The equation was then solved to obtain a cake layer thickness and the permeate flux calculated using equations 4 and 5. The theoretical predictions for the flux improvement on backflushing using this model vs the degree of backflushing defined as the ratio of backflushing time over total cycle time have been included in Figure 10.15 for the CERAMEM LMA and 10.16 for the KOCH CM membrane. In cases where the backflush duration is a small portion of the normal operating time, very little cake removal is expected and this is well predicted by theory as shown in Figures 10.15 and 10.16. As degree of backflushing increases, more permeate is lost in backflushing the membrane and the flux improvement decreases. An optimum exists between these two extremes. The best case of cake layer removal, conducted for the CERAMEM LMA membrane is a 2.5 second backflush in a 120 second total cycle time and for the KOCH CM membranes is a 5 second backflush in a 120 second total cycle time.

For both membranes, theory predicts that the cake layer removal exceeds the cake layer buildup. For conditions of a 115 second operational cycle, followed by a 5 second backflush the following theoretical conditions would exist. For the CERAMEM LMA membrane a cake layer of approximately 1.06 microns would form and a cake layer as thick as 522 microns would be removed. For the KOCH CM membrane a cake layer of 4.16 microns would form and a cake layer as thick as 2,712 microns would be removed. However, the actual experimental data does not support this position. Therefore, while the theory predicts that only a small backflush differential pressure and time of backflushing are required to remove the cake layer it is obviously much more difficult to remove the cake layer from the membrane surface. Depending on the nature of the cake, increasing the backflush differential pressure and time could more effectively remove the cake layer from the membrane surface.

To gain a better understanding of the impact of backflushing it is worthwhile to review the efficiency of backflushing, for varying degrees of backflushing, for the two

membranes. Table 10.3 presents these results. Flux improvement is the ratio of the fluxes, for various backflushed runs, versus the non-backflushed run. For the CERAMEM LMA membrane this flux improvement was determined using the flux ratios in order to eliminate the impact of the continual irreversible membrane fouling. While for the KOCH CM membrane the flux improvement was determined using the fluxes from the various runs, since it did not experience irreversible fouling. These results are also presented graphically in Figures 10.15 and 10.16.

Table 10.3: Backflushing Flux Improvement

MEMBRANE	BACKFLUSH		FLUX IMPROVEMENT	
	Backflush Time / Total Cycle Time	Backflush Fraction $\left(\frac{backflush\ time}{cycle\ time}\right)$	Experimental	Theory
	(sec/sec)	(-)	(%)	(%)
CERAMEM LMA	0/120	0.000	0.0	0.0
	2.5/120	0.021	26.9 ± 3.1	100.0
	2.5/60	0.042	11.8 ± 1.4	96.3
	5/120	0.042	15.6 ± 1.8	95.7
	10/120	0.083	10.8 ± 1.3	87.2
KOCH CM	0/120	0.000	0.0	0.0
	5/120	0.042	14.3 ± 0.4	9.8
	5/90	0.056	13.0 ± 0.4	99.3
	5/60	0.083	15.7 ± 0.5	99.6
	5/45	0.111	8.0 ± 0.2	97.3
	5/30	0.167	2.3 ± 0.1	89.5

Both membranes tend to follow the theoretical trends reasonably well; that is the actual and theoretically predicted optimal backflushes are very close. However, the actual results differ from the theoretical values in a number of manners. First, and most obviously, is the magnitude of the two values, i.e. the actual flux improvement with backflushing is significantly less than expected from the theoretical prediction. As discussed earlier, this is due to the likelihood that the backflushing incompletely removes the cake layer.

The error associated with the experimental flux improvement values is due to the error carried throughout the calculations of these values. For the CERAMEM LMA membrane, due to the irreversible fouling it experienced, it utilized flux ratios to calculate its flux improvement. The percentage error associated with the flux ratios was approximately ± 1.3% therefore resulting in an error of ± 2.5% for the flux improvement values. Whereas the KOCH CM membrane used flux values to determine its flux improvement values and the error associated with these flux values was ± 0.6% and therefore the error associated with its flux improvement values was ± 1.3%.

Secondly, the flux improvement drops off significantly faster, from the optimal degree of backflushing, than predicted. This is related to the first point since backflushing is not as effective as theoretically expected and therefore the time lost for permeate collection, during the conduct of the backflush, is more critical to the overall flux. This is very important when put into the context of how to best improve the impact of backflushing. That is, the ability of backflushing to remove the cake layer is dependent upon the amount of time used to backflush and the backflush pressure. As Figure 10.15 and 10.16 reveal it is very important to keep backflushing times as short as possible in order to maximize permeation time.

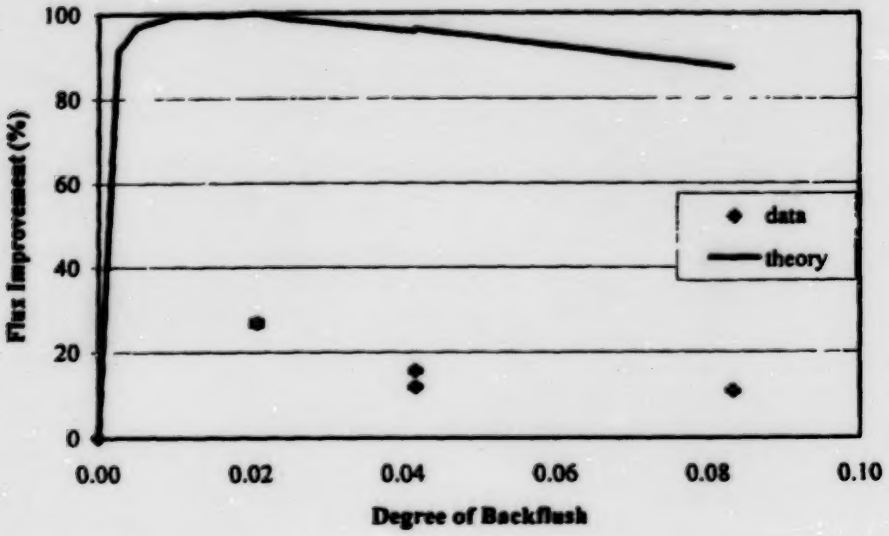

Figure 10.15: Flux Improvement versus Backflushing for CERAMEM LMA Membrane, New Bilge Water

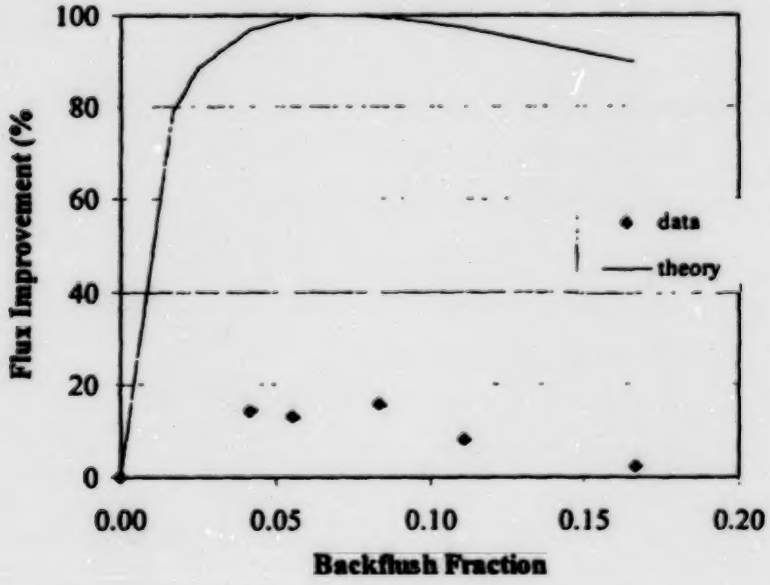

Figure 10.16: Flux Improvement versus Backflushing for KOCH CM Membrane, New Bilge Water

10.2.5 Effect of Membrane Pre-Treatment

Reviewing the case of the treatment of bilge water contaminated with used lube oil (used bilge water) with the KOCH CM membrane, Figure 10.17, at first glance it would appear to disprove the above findings. However, as stated earlier these experimental runs were conducted with a 100 micron pre-filter and this pre-filter performed some pretreatment. In order to determine if the pre-filter provided any impact upon bilge water treatment Figure 10.18 plots the 24 hour flux values in the sequential order that they experimental runs were performed. As seen from this graph the flux continually increases, until the final run, for which the pre-filter was removed.

Additionally, the flux values are worth noting. The first experimental run, with bilge water contaminated with used lube oil, was the run using a 5 second backflush. From Figure 10.17 it can be seen that this run produced a flux, after 24 hours of operation, of approximately 165 L/m^2/hour. This compares to a flux value, after 24 hours of operation, of approximately 162 to 175 L/m^2/hour for various degrees of backflushing, for bilge water contaminated with new lube oil. From Figure 10.17 it can be seen that for the following runs, with used bilge water the flux values continued to increase, until the pre-filter was removed for the final run, with no backflushing.

After four experimental runs, approximately 100 hours of operation, the flux had risen from 165 L/m^2/hour to over 250 L/m^2/hour. Therefore it can be seen that the pre-filtration provided an extremely effective means of enhancing the membrane flux. With the exception of the backflushing none of the operational parameters were altered during these runs.

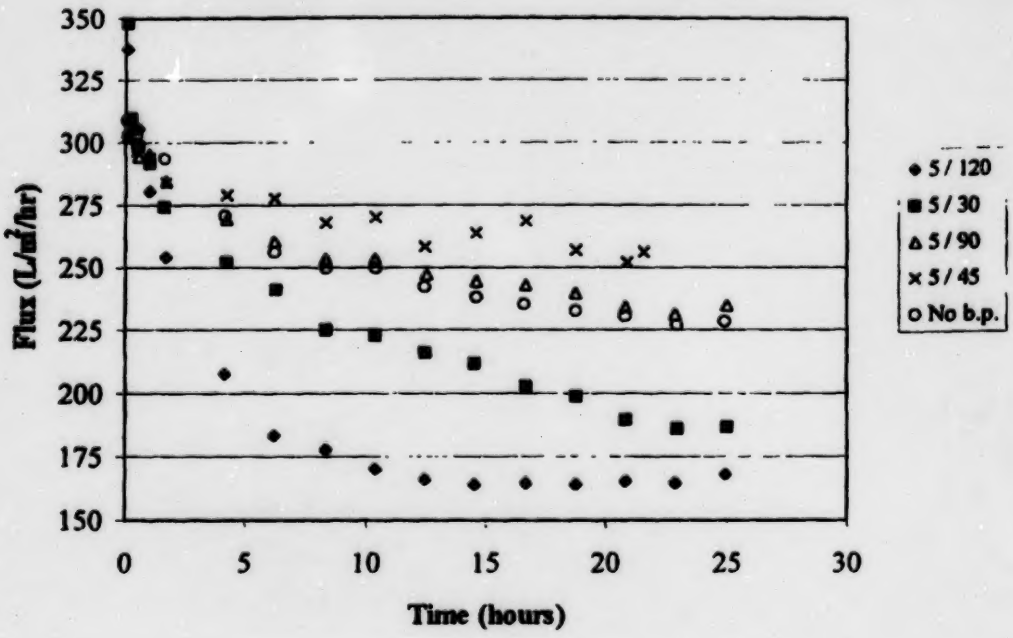

Figure 10.17: KOCH CM Membrane, Used Bilge Water, 206KPA, Varying Backflushes

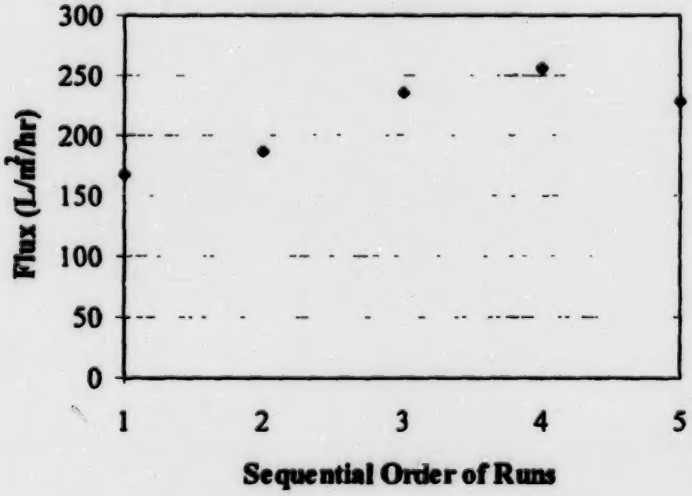

Figure 10.18: KOCH CM Membrane, 206KPa,
Sequential Order of Experiment Used Bilge Water Runs

A visual inspection of the pre-filter revealed that it was heavily fouled with oil and soot. Additionally, when the pre-filter was drained it had collected free oil in its inner chamber; the bilge water flowed into the inside of the filter and then through the filter. Therefore, it appears that the pre-filter provided the oil emulsions with a coalescing medium, causing an increased membrane flux as the oil and particulate content of the bilge water were reduced.

10.2.6 Permeate Quality

Tables 10.4 and 10.5 provide the oil content values of the permeate, for the various experimental runs. As seen from these tables the permeate quality appears to be reasonably consistent and independent of the operational parameters and bilge water conditions that were altered, such as trans-membrane pressure, degree of backflushing, other operational parameters or the treatment of bilge water containing either new or used lubricating oil.

Table 10.4: CERAMEM LMA Membrane Permeate Quality

(Pore Radius of 0.005 microns)

Pressure (KPa)	Backflush - backflush per total cycle time (sec/sec)	Bilge Water	SPE C18 Oil Content (ppm) ± 13.7 ppm	Oil Content hexane extractable equivalent* (ppm)
206	5/120	Used oil	19.8	11
206	10/120	Used oil	16.2	9
206	2.5/120	Used oil	46.0	25
206	5/120	Used oil	33.3	18
206	5/120	Used oil	1.7	1
220	5/120	New oil	33.5	18
220	10/120	New oil	29.7	16
220	2.5/120	New oil	14.4	8
220	2.5/60	New oil	23.7	13
220	5/120	New oil	4.3	2
206	5/120	New oil	23.1	12
220	No backflush	New oil	55.0	30
206	No backflush	New oil	9.8	5

* Hexane extractable equivalent SPE C18 x 0.54 see SECTION 11 of this report.

Table 10.5: KOCH CM Membrane Permeate Quality (MWCO of 50,000 Daltons)

Pressure (KPa)	Backflush - backflush per total cycle time (sec/sec)	Bilge Water	SPE C18 Oil Content (ppm) ± 13.7 ppm	Oil Content hexane extractable equivalent* (ppm)
206	5/30	New oil	19.1	10
206	5/60	New oil	14.2	8
206	5/90	New oil	14.8	8
206	5/45	New oil	19.3	10
206	No backflush	New oil	14.1	8
206	5/120	New oil	8.9	5
186	5/120	New oil	12.9	7
206	5/30	Used oil	22.6	12
206	5/90	Used oil	28.7	15
206	5/45	Used oil	12.1	7
206	5/60	Used oil	19.4	10
206	No backflush	Used oil	8.8	5
206	No backflush	Used oil	19.8	11
206	5/120	Used oil	20.6	11

* Hexane extractable equivalent SPE C18 x 0.54 see SECTION 11 of this report.

Additionally, there did not appear to be a significant difference between the permeate oil content from the CERAMEM LMA and KOCH CM membranes. The average permeate oil content, for the CERAMEM LMA and KOCH CM membranes, were 23.9 ppm and 16.8 ppm, respectively. The difference in these two values is within the error attributed to the solid phase extraction method for the determination of oil content. On several occasions, five out of thirteen did the CERAMEM LMA membrane not meet the hexane equivalent discharge concentration of 15 mg/L. On the other hand the KOCH CM membrane met the requirement at all times coming close to exceeding it on two out of 14 trials.

Regarding the permeate oil content it is important to quantify the method used since "oils and greases" are defined by the method used for their determination (Greenberg et al., 1992). Unfortunately, the Canada Shipping Act does not provide a clear definition of "oil". Discussions with various Canadian naval authorities have confirmed that the new membrane based Oily Water Separator (OWS) System and the existing SAREX Coalescing OWS System have both successfully been certified by Transport Canada and International Maritime Organization. The new membrane based OWS being acquired by the Canadian Navy uses virtually the same membrane as the KOCH CM membrane that was tested; the same material, configuration and MWCO.

10.3 CONCLUSIONS

Permeate Quality

From the pilot scale studies it was observed that permeate quality was independent of membrane operational parameters, including the membrane used, and bilge water composition. The average permeate qualities based on SPE C18 results were 24 ppm and 17 ppm, for the CERAMEM LMA and KOCH CM membranes respectively; however the error associated with the solid phase extraction method is sufficient to neither confirm nor deny the production of an acceptable permeate quality. Based upon the conversion factor of 0.54 to convert SPE C18 extraction to hexane extractable oil and grease (see SECTION 11) these values would be 12 and 9 mg/L respectively which meet the 15 mg/L hexane extractable regulations for overboard discharge.

Fouling

An important component of system efficiency is a membrane's ability to resist fouling and to regain its initial flux after it has experienced fouling. The amount of irreversible fouling associated with the membranes was determined. This was assessed by comparing the pure water permeate flux of the membranes before and after bilge water treatment. With respect to irreversible fouling, the KOCH CM membrane proved superior to the CERAMEM LMA membrane. The KOCH CM membrane did not appear to experience any appreciable flux decline over the course of its usage. However, the CERAMEM LMA membrane experienced longer term flux decline. This was noted in both the reduction in its pure water permeate flux rate prior to and after its series of experimental runs and a continual decline, over each experimental run, in its initial bilge water flux rates. Additionally, as determined by examination of the backflushing efficiency it appears that the cake layer strongly adheres to both membranes, evidenced by the observation that the backflushing did not provide the degree of flux improvement theoretically suggested.

Backflushing

The effect of backflushing was primarily examined from its impact upon flux enhancement for the treatment of bilge water, consisting of new lubricating oil. Backflushing resulted in a marginal increase in flux capacity. Further investigation into the (theoretically predicted) benefits of backflushing revealed that the pressure and duration of the applied backflushes, used in the experimental runs, should have been sufficient to completely remove the cake layer; however, this was not observed. This over prediction could be attributed to the oil emulsions within the cake layer adhering to the surface of the membrane.

Comparison of identical degrees of backflushing, but differing backflushing cycles – i.e. CERAMEM LMA membrane with 2.5/60 and 5/120 backflushing runs – revealed an improvement in backflushing effectiveness for the larger backflush time. This lends credence to the belief that oil may be adhering to the membrane surface as the increased backflush duration could result in increased "scouring" of oil from the membrane surface. Increasing the backflushing efficiency could be accomplished by two means, increasing the backflush pressure or increasing the duration of backflush.
Additionally, the optimization of backflushing was investigated. While the theory under predicted the efficiency of backflushing it did provide good prediction of the optimal backflushing regime, i.e. duration of backflushing per total cycle time.

Pre-Treatment

Pre-treatment, prior to membrane separations, is commonly accepted engineering practice for a number of reasons, the least of which is the prevention of system fouling by relatively large particles, by a membrane's standard. However, during the experimental runs with the KOCH CM membrane, for the treatment of used bilge water, it was shown that a pre-filter provides a significant improvement in the membrane flux where permeate flux improved after each run.

P515557.PDF [Page: 141 of 154]

Generally over time a membrane is expected to foul, resulting in flux degradation. However, with the insertion of the pre-filter, flux improved from 165 to 250 $L/m^2/hr$, over a period of approximately 100 hours (4 experimental runs).

The filter appeared to provide a coalescence medium for free and emulsified oil, as evidenced when the filter was drained at the end of the experimental runs. The filter contained significant amount of free oil that was readily discharged from the filter.

SECTION 11 The Determination of Oil and Grease in Water.

The definition of oil and grease with respect to water and wastewater treatment is rather vague. The term "oil and grease" applies to a wide variety of organic substances including hydrocarbons, esters, oils, fats, waxes and high molecular weight fatty acids (Sawyer et al., 1994). Four standard methods, based upon 1,1,2-trichloro-1,2,2-trifluorethane (Freon-113) extraction exist, and each of these methods extract "oils and greases" from water to differing degrees and therefore each method provides different results. This is critical, as it is necessary to identify the method of "oil and grease" determination being used when identifying the oil and grease content in water. Unfortunately, neither the Canada Shipping Act nor the Arctic Waters Pollution Prevention Act identifies a method for oil and grease determination.

The four standard methods for oil and grease testing all rely upon an initial extraction from water by Freon-113. However, the use of Freon-113 is prohibited by the Montreal Protocol. Therefore Freon-113 extraction could not be used for the extraction of oils and greases from water and an alternative method of testing had to be identified. In lieu of Freon-113 the US EPA has authorized the use of hexane liquid-liquid extraction (EPA Method 1664). In fact, originally both hexane and Freon-113 were listed as acceptable solvents for oil and grease extraction, however Freon-113 was the preferred solvent as it is a lesser explosion hazard (Sawyer et al., 1994).

Hexane liquid-liquid extraction was previously used but the presence of any surfactants (which are likely to be present in membrane permeate) would lead to the formation of an emulsified layer between the hexane and water phases. This difficulty with hexane liquid-liquid extraction has been documented and solid phase extraction (SPE) has since replaced many liquid-liquid extraction methods for the determination of organics in solution (Stone, 1998). Specifically, reverse-phase SPE has been used to remove non-polar compounds from polar compounds, such as water (Beney et al., 1996). In a study comparing the effectiveness of oil and grease extraction, for a variety of wastewaters, using octadecyl (C_{18}) reverse phase SPE and hexane liquid-liquid extraction: It was found

P515557.PDF [Page: 143 of 154]

that the SPE extraction had an average recovery of 107% ± 76% while the hexane liquid-liquid extraction had an average recovery of 100% ± 121% (Stone, 1998).

EPA Method 1664 permits the use of alternate techniques provided they can predict hexane extractable oil and grease. This allows for the use of a conversion factor in relating the results of a SPE method to the results that would be obtained were hexane used as an extractant. Accordingly, it was decided to study the possibility of using SPE techniques to determine the oil content of bilge water.

A complication in both methods arises when brines are tested. The presence of salt transferred in small quantities in the extractant phase will be counted as oil in the subsequent gravimetric test. This is documented in a series of questions and answers provided by the EPA to the implementation of EPA Method 1664. The use of anhydrous sodium sulfate is expected to eliminate this problem as it removes salts along with water. It is recommended by the EPA to reprocess samples should water by-pass the anhydrous sodium sulfate. In a previous trial, the authors found that reprocessing of samples imparted considerable error in the measurement of oil and grease. In this section, salts were not added to the solution in order to eliminate a potential interference in the gravimetric technique.

Study of various commercially available sorbents to be used in the SPE technique

The nature of the extractant phase in the hexane and the SPE techniques are very different and this is expected to affect the recovery of oil and grease from wastewater. The amount of oil extracted will also depend on the presence of surfactants in the wastewater. The problematic stability of emulsions at the hexane-water interface attests to the limited ability of hexane to destabilize emulsions. The following study was performed to determine the effect of mechanical and chemical emulsions on the ability of Hexane and various SPE's to extract oil and grease.

Tests using an oil/detergent mix in the absence of salts

Method

A dilute synthetic bilge water solution was prepared. The solution contained diesel fuel, used oil, hydraulic oil, detergent, Cleanbreak, and corrosion inhibitor. A total of 200L of solution was prepared having a total oil concentration of 88 mg/L. The solution was diluted to an oil concentration of 22 mg/L of oil. The solution was milky and formed a stable emulsion that did not produce a sheen on its surface over a three-week period. As previously mentioned, salts were not added to the solution in order to eliminate a potential interference in the gravimetric technique. In this section, tests were performed after the oily water was circulated for 15 minutes and allowed to sit for one hour.

The basic extraction method consisted in a three-step procedure. The first step was to condition the SPE tubes. This consisted in flushing them with 5mL of hexane and 5 mL of methanol, the solvents used to extract the oil from the SPE tubes. Once the tubes were conditioned the bilge water permeate was extracted by suction. The sorption of the oil onto the SPE packing was evidenced by the formation of a ring of extracted oil. The final step was extracting the sorbed oil from the SPE tubes by washing them with organic solvents. Five 5mL washes of both hexane and methanol were conducted for each SPE tube. The solvents were forced through the packing by air pressure. The extracted material was collected in aluminum weighing dishes and the organic solvents evaporated in ambient air.

Results

The amount of oil extracted and the % oil recovery using various SPE columns can be found in Table 11.1. In order to limit the loading on the SPE only 0.5 L was passed through the column. The standard amount of 1 L of oily water was treated in the EPA test as described in Method 1664.

Table 11.1. SPE and EPA 1664 oil recovery based on a total of 22 mg/L of oil and grease. SPE tubes containing 500mg of adsorbent were used (SUPELCO, Oakville, Ontario).

SPE – Hexane	mg recovered per 500 ml treated	% Recovery based on 22 mg/L oil and grease
LC-ALUMINA-A	6.4	58
LC-ALUMINA-B	4.8	44
LC-ALUMINA-N	6.5	59
LC-CN	5.1	46
LC-FLORISIL	4.3	39
LC-SI	3.5	32
ENVI-8	5.4	49
EPA 1664-A	10.4 (1 L)	47
EPA 1664-B	9.5 (1 L)	43
EPA 1664-C	9.9 (1 L)	45
LC-18-A	9.1	83

These recoveries were plotted in Figure 11.1 below. Maximum recovery was obtained using the LC18 (octadecyl (C_{18})) SPE. Other extractants produced recoveries ranging from 32 to 59 %. When liquid-liquid hexane extraction was used according to EPA Method 1664 it was found to give recoveries of 43 to 47 %. This is nearly half of that obtained using the C18 SPE.

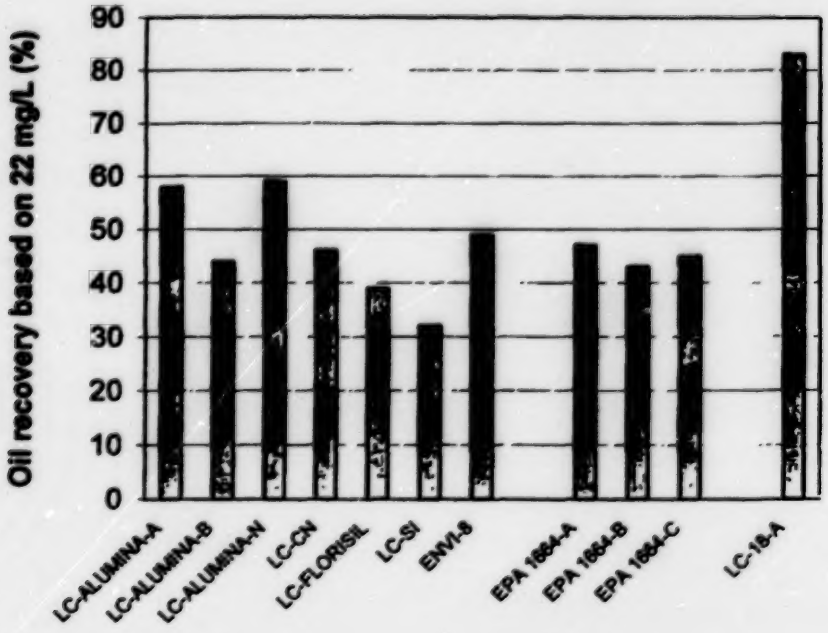

Figure 11.1. Oil recovery using various SPE sorbents.

The EPA suggests that for a known effluent, alternative methods can be correlated to Method 1664 using a simple factor. A factor of 0.54 could be used to relate the LC18 SPE results to the result anticipated using EPA Method 1664.

The results obtained using other sorbents such as alumina-B, LC-CN, ENVI-8 are quite interesting as they are very similar to those obtained using hexane extraction. Table 11.2 below lists the conversion factors that when multiplied by the SPE oil result will give the amount of oil that would be extracted using hexane. The ability of LC18 to destabilize emulsions is evident by the comparison of results obtained with liquid-liquid hexane extraction. Extraction with alumina-B, and other sorbents that apparently do not destabilize emulsified oil is a better predictor of hexane extractable oil than the octadecyl sorbent. If a sorbent is to be utilized in this application where the goal is to best represent

hexane extraction then the better sorbents are the ones that do not destabilize chemical emulsions.

Table 11.2. Conversion factors from SPE result to hexane extraction based on a 45% oil recovery for EPA 1664.

SPE – Hexane	Conversion factor
LC-ALUMINA-A	0.78
LC-ALUMINA-B	1.02
LC-ALUMINA-N	0.76
LC-CN	0.98
LC-FLORISIL	1.15
LC-SI	1.41
ENVI-8	0.92
LC-C18	0.54

Tests to determine the effect of oil loading on the SPE

Method

Using the octadecyl (C_{18}) reverse phase solid phase extraction a number of extractions were conducted with varying amounts of new diesel lubricating oil, ranging from 22 to 141 mg/L. The extraction procedure was identical to the previously described method. As in the previous test the sorption of oil onto the SPE packing was evidenced by the formation of a ring of extracted oil. The final step was extracting the sorbed oil from the SPE tubes by washing them with organic solvents. Five 5mL washes of both hexane and methanol were conducted for each SPE tube. The solvents were forced through the packing by air under pressure. The extracted material was collected in aluminum weighing dishes and the organic solvents evaporated in ambient air.

Results

Figure 11.2 presents these results. From these trials it was found that the oil recovered, through this solid phase extraction method, related to known quantity of oil in accordance with the following equation and 95% confidence interval:

$$\text{oil in water} = 1.25(wtSPE) - 9.9 \pm 13.7 \quad \text{mg/L} \qquad (1)$$

Where *wtSPE* is the quantity of recovered oil, in mg, as removed from the octadecyl reverse phase material. The reproducibility of this method is poor, but it is comparable to that of hexane liquid-liquid extraction, as identified in by Stone, 1998.

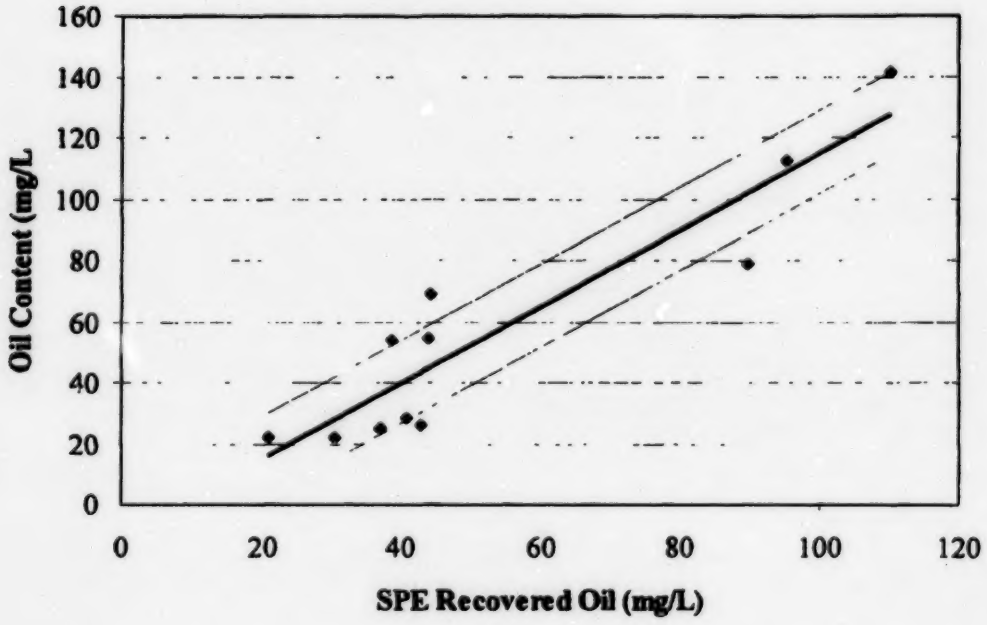

Figure 11.2: Results of SPE Trials for Oil Extraction from water in the absence of salts or detergents.

To achieve these recovery levels two SPE cartridges were used in series, with the first SPE tube extracting approximately twice as much oil as the second SPE tube. The results using the diluted bilge water cocktail described in the previous section are somewhat

P515557.PDF [Page: 149 of 154]

similar although the oil recovery using C18 SPE was 83 %. This result falls within the margin of error given in Figure 11.2.

Conclusions

When using SPE techniques, the amount of oil extracted is highly dependent on the type of sorbent used in the extraction process.

In a mixed mechanical/chemical emulsion the amount of oil extracted will depend on its affinity for free oil and its ability to destabilize the chemical emulsion. The sorbent found to extract the greatest amount of oil from a mixed oil/detergent system representing bilge water in the absence of salt water was octadecyl LC-C18 8 (SUPELCO, Oakville, Ontario).

The amount of oil extracted by the LC-C18 sorbent was greater than that extracted using hexane (EPA Method 1664). Other sorbents were not as effective in removing oil from the mixed system. Sorbents such as alumina-B, LC-CN and ENVI-8 (SUPELCO, Oakville, Ontario) were better predictors of hexane extractable oil than the LC-C18 octadecyl sorbent. If a sorbent is to be utilized in an application where the goal is to best represent hexane extraction then the better sorbents are the ones that do not destabilize chemical emulsions as hexane is non-polar and should not extract chemical emulsions.

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This study is aimed at determining the phenomena that affect the treatment of bilge water using membrane based oily water separators. The results of the study are presented here as two separate papers. One paper discusses the most problematic particle sizes in the treatment of bilge water by synthetic membrane technologies while the other discusses the effects of shear and settling on bilge water treatment by ultrafiltration. The report also contains a section on the use of ultrafiltration membranes in oily water separators that elucidates the effects of small particles of soot in the bilge water on membrane performance and showed that the permeation of water through the membrane was entirely cake/gel limited. The thickness or resistance of this cake/gel layer was influenced by the quantity and size distribution of these soot particles in the influent stream. The work identifies the most effective membrane pore size to use in purifying bilge water which is contaminated with used diesel lubrication oil.

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